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CANADIAN WILTSHIRE BACON XXVIII. CHLORIDE SHIFT IN CURED PORK¹

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Abstract

Carefully conducted flavor tests and chemical analyses for chloride ion showed that bacon of the Wiltshire type increased in saltiness and water extractable chloride during storage. Enzyme digests of freshly cured pork gave higher chloride recoveries than those obtained in water extraction procedures. On the other hand, recovery of sodium ion in freshly cured material was identical by water extraction, enzyme digestion, or a wet ashing procedure. These results show that the chloride ion is bound by the muscle constituents and that it can be released by enzyme action. This mechanism would explain the increase in saltiness observed in stored bacon.

Introduction

The most serious complaint against Canadian bacon exported to England is its excessive saltiness. This has been supported by flavor tests conducted in England (7). Although it is generally recognized that curing practice is largely responsible for the saltiness of the product, commercial operators have claimed that bacon of the Wiltshire type increases in saltiness during storage. If this is true, then the saltiness of Canadian bacon increases before it is consumed in England. Hence it was thought advisable to investigate the effect of aging on saltiness and to study some of the changes taking place in the muscle tissue.

Experimental and Results

The material in the first experiment consisted of rib-in export backs from 20 hogs. The backs were cut in half and two half-backs allotted at random to each experimental condition. The half-backs were cured to contain 0.2% nitrate at sodium chloride levels of 2, 3, 4, 5, and 6%, and 0.1% nitrate at sodium chloride levels of 2, 4, and 6%. For the material to contain 0.2% nitrate, the pump pickle contained 30% sodium chloride, 1.5% nitrate, and 0.05% nitrite, while the cover pickle contained 28% sodium chloride, 1.5% nitrate, and 0.05% nitrite. Material to contain 0.1% nitrate was cured in similar curing pickles except that the nitrate concentration was reduced to

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0.5%. Different sodium chloride levels were obtained by varying the amount of pickle pumped into each half-back and by the time in cure. The material was cured in small tanks for two to four days at 4.4° C. (40° F.) and at a pickle to meat ratio of 20 gal. per 100 lb.

After removal from cure, the pieces were wrapped in waxed paper, over-wrapped in brown kraft, and stored at -1.1° C. (30° F.). Samples were removed from storage at 0, 6, 12, 18, and 24 days and prepared for chemical and biological determinations. Half-backs were sampled as follows: bones were removed and the back cut into slices $\frac{1}{4}$ in. thick. The slices were then randomized into three lots for chemical analyses, taste panel assessments, and vitamin analyses. Chemical analyses were also done on the cooked samples. The work on the vitamin analyses will be reported in a separate paper (1). The material for chemical and vitamin analyses was trimmed free of most of the fat, minced three times in a food chopper, frozen at -40° C., and stored at that temperature until required for analysis. After the material was thawed, chloride (6), nitrate (4), and moisture contents (6) were determined. Flavor was determined as follows: small pieces of the meat were trimmed free of fat and grilled at 260° C. (500° F.) on a wire screen for six minutes (three minutes on each side). Saltiness was assessed on the following scale: -1 to -5, deficiency; 0, ideal; +1 to +5, excess saltiness. The scoring panel of 15 people was required to score no more than four samples in any morning or afternoon.

Chloride and nitrate contents of the lean meat for each experimental cure, averaged over all storage times, are given in Table I. It is evident that a range of salt concentrations from 3.8 to 5.7% and two levels of nitrate, 0.1% and 0.2%, were obtained in curing the material.

TABLE I

MEAN CHLORIDE AND NITRATE CONTENTS OF WILTSHIRE BACON FROM SEVERAL CURES, AFTER STORAGE AT -1.1° C. (30° F.) FOR 24 DAYS

(Values averaged over all storage times)

Desired nitrate level, %	Desired chloride level, %	Chloride, ^a %		Nitrate, ^a %	
		Raw	Cooked	Raw	Cooked
0.2	2	3.86	6.29	0.16	0.27
	3	4.74	7.05	0.20	0.30
	4	5.01	7.60	0.24	0.37
	5	5.27	7.70	0.21	0.34
	6	5.60	8.13	0.25	0.38
0.1	2	4.35	6.52	0.06	0.09
	4	5.07	7.73	0.06	0.10
	6	5.70	8.53	0.07	0.11
Necessary difference ^b		0.58	0.74	0.027	0.027

^a Calculated as the sodium salt.

^b Necessary difference to exceed the 5% level of statistical significance.

As it is difficult to cure any two pieces of meat to contain exactly the same salt content, the difference between duplicate samples may be large. Hence statistical analyses of the data were employed to establish the significance of any trends obtained in storage. Table II shows the results of an analysis of

TABLE II

ANALYSIS OF VARIANCE FOR THE EFFECTS OF STORAGE ON THE CHLORIDE, NITRATE, AND MOISTURE CONTENTS AND THE FLAVOR OF WILTSHIRE BACON STORED FOR 24 DAYS AT -1.1°C . (30°F .)

Source of variance	Degrees of freedom	Mean square						
		Chloride		Nitrate		Moisture		Flavor
		Raw	Cooked	Raw	Cooked	Raw	Cooked	
Cures	7	3.8**	5.9**	0.066**	0.155**	0.7	16.0	1.50**
Time	4	2.1**	5.2**	0.008**	0.039**	2.6	1.7	2.20**
Cures \times time	28	0.4	0.6	0.001	0.003	0.8	10.4	0.14
Between duplicates	40	0.4	0.7	0.002	0.002	1.4	25.9	0.27

** Indicates 1% level of statistical significance.

variance: the time of storage had significant effects on the chloride and nitrate contents and on flavor, the moisture content was unaffected, and all the salt levels behaved similarly. The magnitude and direction of the significant effects are given in Table III. Flavor scores showed a significant

TABLE III

EFFECTS OF TIME OF STORAGE ON THE MEAN CHLORIDE AND NITRATE CONTENTS AND FLAVOR SCORE OF WILTSHIRE BACON STORED AT -1.1°C . (30°F .) FOR 24 DAYS

(Values averaged over all cures)

Time, days	Chloride, ^a %		Nitrate, ^a %		Flavor score ^b
	Raw	Cooked	Raw	Cooked	
0	4.44	6.68	0.13	0.17	0.7
6	4.73	7.04	0.14	0.26	0.9
12	5.09	7.66	0.17	0.23	1.3
18	5.15	7.82	0.16	0.27	1.6
24	5.35	8.03	0.18	0.30	1.6
Necessary difference ^c	0.46	0.56	0.027	0.024	0.4

^a Calculated as the sodium salt.

^b Saltiness ratings only.

^c Necessary difference to exceed the 1% level of statistical significance.

increase in saltiness during storage, first evident after 12 days. This coincided with significant increases in chloride and nitrate contents of both the cooked and uncooked meat. From these results the increase in saltiness on storage appears to be real and substantial.

Comparison of Analytical Methods

It was necessary to consider the analytical methods involved and to check the results of the previous experiment by employing another analytical procedure. The investigations of White (6) on cured meat showed that ashing the meat by the A.O.A.C. method and titrating by the Volhard procedure (3) produced lower chloride values than extracting the meat with hot water and titrating by the Mohr procedure (6). There are two possible explanations for these results; underestimation of chloride by loss of chlorine during ignition of the meat in the ashing procedure or the overestimation of chloride ion by titration of materials other than chloride in the water extract of the meat. The latter was checked by adding known amounts of pure sodium chloride to water extracts of fresh pork. Complete recoveries of the chloride ion were obtained. Therefore it was assumed that, owing to loss of chlorine during ignition, the ashing procedure underestimates chloride content and that water extraction and direct titration is the better procedure.

The increase in chloride content of stored bacon was rechecked by the ashing and water extraction procedures. The results are given in Table IV.

TABLE IV

THE ESTIMATION OF SODIUM CHLORIDE IN WILTSHIRE BACON STORED FOR 0 AND 24 DAYS AT -1.1°C . (30°F .) BY DRY ASHING AND WATER EXTRACTION PROCEDURES

(Means of duplicate determinations)

Sample No.	Sodium chloride, %			
	Dry ashing		Water extraction	
	0 days	24 days	0 days	24 days
1	2.1	3.3	2.4	3.5
2	3.5	4.7	3.6	5.1
3	4.8	5.8	4.9	6.2

The chloride content as determined by the ashing procedure was lower than that determined by water extraction. This is in agreement with the previous results reported by White (6). Although the chloride values obtained by the two methods were different the increase in chloride content on storage of bacon was evident by both procedures. Therefore the increase in saltiness of bacon on storage does not depend on the analytical procedure used to estimate the chloride ion.

Diffusion of Chloride or Moisture from Fat to Lean

As only the lean meat had been analyzed it was possible that chloride and nitrate had diffused from the fat to the lean. This was investigated but since nitrate is unstable owing to bacterial action, only changes in the chloride were followed.

This experiment employed six export backs divided into 30 pieces. The pieces were cured to give sodium chloride contents of 2, 4, and 6%, then stored and sampled as in the previous experiment. Chloride and moisture contents were determined on the fat and lean portions of each piece. Moisture content in the fat and lean and chloride content in the lean were determined as previously described (6). Chloride content in the fat was determined according to the method of the A.O.A.C. (3) in which the sample is ashed, leached with hot water, and the chloride of the extract determined by the Mohr procedure.

Chloride and moisture contents of the fat and lean meat for each cure, averaged over all storage times, are given in Table IV. It is evident that only small amounts of chloride and moisture diffuse into fat during curing. Statistical analysis of the data shows that the time of storage had a significant effect on the chloride content of both lean and fat (Table V). As pork fat

TABLE V
CHLORIDE AND MOISTURE CONTENTS OF THE LEAN AND FAT OF WILTSHIRE
BACON STORED AT -1.1°C . (30°F .) FOR 24 DAYS
(Mean values averaged over all other conditions)

Desired chloride levels, %	Lean meat		Fat	
	Chloride, %	Moisture, %	Chloride, %	Moisture, %
2	2.82	71.6	0.37	7.68
4	4.44	71.2	0.59	7.52
6	6.10	70.9	0.63	7.33
Necessary difference ^a	0.56	0.86	0.14	1.02

^a Necessary difference to exceed the 1% level of statistical significance.

contains appreciable amounts of connective tissue, it is not surprising that it exhibits somewhat the same behavior as lean meat. It is evident that the increase in water extractable chloride could not be attributed to diffusion of the chloride or moisture from the fat to the lean.

Release of Bound Chloride by Enzymes

The increase in water extractable chloride on storage may be explained by fixation of a portion of the chloride by the freshly cured muscle and subsequent release of chloride through enzyme action, or otherwise. As it was possible that fixation of either the sodium or chloride ion, or both, may have occurred, both sodium and chloride were determined on freshly cured pork in the next experiment.

Freshly cured backs were trimmed free of fat and bone, minced, and samples subjected to water extraction, enzyme digestion, and wet ashing procedures. Water extraction was carried out by a previously described method (6). In the enzyme digest procedure, 10 gm. of meat was digested for 18 hr. at 37° C. with 0.2 gm. of papain and 0.2 gm. of takadiastase in 100 ml. of solution adjusted to pH 4.6. Wet ashing was done with concentrated sulphuric and nitric acids. Chloride was determined by the Mohr procedure and sodium by precipitation as sodium zinc uranyl acetate (5, p. 878). From Table VI, it is

TABLE VI

EFFECTS OF STORAGE ON THE CHLORIDE AND MOISTURE CONTENTS OF THE FAT AND LEAN PORTIONS OF WILTSHIRE BACON STORED AT -1.1° C. (30° F.) FOR 24 DAYS

(Mean values averaged over all other conditions)

Time, days	Lean meat		Fat	
	Chloride, ^a %	Moisture, %	Chloride, ^a %	Moisture, %
0	3.64	72.3	0.37	7.31
6	4.21	71.5	0.41	7.64
12	4.85	70.6	0.48	7.08
18	4.62	71.0	0.67	8.43
24	4.94	70.7	0.68	7.05
Necessary difference ^b	0.72	1.11	0.14	0.39

^a Calculated as the sodium salt.

^b Necessary difference to exceed the 1% level of statistical significance.

evident that the recovery of the sodium was similar by water extraction, enzyme digestion, or wet ashing procedures, but that digestion with papain and takadiastase gave higher recoveries of chloride than the water extraction procedure. These results show that the chloride is bound by the muscle tissues, that it can be released by enzyme action, and that the sodium ion is not bound.

TABLE VII

CHLORIDE AND SODIUM CONTENTS OF FRESHLY CURED WILTSHIRE BACON BY DIFFERENT METHODS OF ANALYSIS

Sample No.	Sodium, %			Chloride, %		Chloride, % Difference between enzyme digest and water extract
	Water extract	Enzyme digest	Wet ash	Water extract	Enzyme digest	
1	0.73	0.80	0.81	1.22	1.52	0.30
2	0.94	0.95	0.93	1.48	1.96	0.48
3	2.05	2.06	2.06	3.19	3.63	0.44

Discussion

The increase in saltiness in cured pork may be satisfactorily explained as follows: while pork is curing in brine solution, some of the chloride ions are bound by the muscle tissues while the sodium ions remain in the outer tissue fluid with the excess sodium chloride. When the cured pork is stored, bacterial or autolytic enzymes or both break down the muscle tissue and the chloride is released. The freed chloride then reunites with the sodium to form sodium chloride. If it is assumed that the bound chloride is not released on mastication, this mechanism satisfactorily explains the increase in saltiness that occurs in stored bacon. An increase in nitrate also occurred during storage, and it is possible that the nitrate ion is behaving similarly to the chloride ion. This would further enhance the saltiness during storage, as it has been shown that sodium nitrate imparts a salty flavor to cured products (2). As the concentrations of potassium and other ions were not determined, no calculations have been made to determine the amount of chloride bound by the muscle tissue or accounted for as sodium chloride. More work is required to ascertain the concentration of chloride that is bound by the muscle tissue, and the factors governing the reaction.

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CANADIAN WILTSHIRE BACON

XXIX. CHANGES IN THE THIAMINE, RIBOFLAVIN, AND NIACIN CONTENTS PRODUCED BY CURING, STORAGE, AND COOKING¹

BY PAUL R. GORHAM²

Abstract

Significant amounts of thiamine and niacin, but not of riboflavin, were lost during the process of curing pork half-backs in brine pickle on a semicommercial scale. This loss was not related to the final chloride or nitrate content of the meat. Cured half-backs stored at 30° F. (-1.1° C.) for 24 days lost significant amounts of thiamine and riboflavin, but the niacin content remained unchanged. Curing caused a significant increase in the percentage of niacin retained after cooking. During the storage of cured half-backs, the percentage of thiamine retained after cooking increased significantly.

Introduction

As part of an extensive series of investigations of Canadian Wiltshire bacon aimed at improving the quality of the product being shipped overseas, a study was undertaken of the losses of three of the more important B-vitamins arising from the use of different curing pickles, storage, and cooking.

Jackson *et al.* (5) found that with the "wet cure" method of processing bacon the loss of thiamine and niacin exceeded that of riboflavin, while in "dry cured" bacon the greatest loss occurred with riboflavin. Little or no information was available on changes in the B-vitamin content of bacon caused by storage or cooking.

Materials and Methods

In the preceding paper (2) full details have been given of the curing, storage, cooking, and sampling of the 80 half-backs of pork from which samples were obtained for vitamin analyses. These half-backs were cured to produce final chloride contents ranging from 2 to 6% at nitrate levels of 0.1% and 0.2%. Duplicate half-backs from each of the eight cures were withdrawn from storage at 30° F. every six days. Fat and fiber were trimmed away and the lean meat uniformly sliced. The slices from each half-back were distributed at random into four equal lots, of which two were available for vitamin analyses. Of these, one lot was thoroughly ground and mixed by two passages through a meat grinder, while the slices in another lot were cooked by broiling in a domestic electric oven for three minutes on each side and then ground. The ground samples were stored at -40° F. pending analysis.

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Four uncured half-backs were treated in a comparable manner to provide samples of fresh and cooked pork for analysis.

Samples were withdrawn from -40°F . and allowed to thaw for 24 hr. at 40°F . A 15 gm. portion of uncooked or a 10 gm. portion of cooked material was extracted with papain and takadiastase and made up to a volume of 200 ml. (7). A dilution of 25 ml. per 100 ml. was used for the assay of thiamine by a modification (11) of the thiochrome method (4, 10). Riboflavin was assayed fluorometrically, using the antimony trichloride-ethanol procedure (7). A dilution of 2.5 ml. per 100 ml. was used for the microbiological assay of niacin by the method of Krehl, Strong, and Elvehjem (6).

Moisture determinations, made on the ground samples by vacuum-drying at 100°C . (2), were used to calculate the results on a moisture-free basis. Changes caused by cooking were expressed as the percentage vitamin retained.

Results

Fresh pork was found to contain, on the average, 66 μgm . of thiamine, 6 μgm . of riboflavin, and 220 μgm . of niacin per gram dry weight. As was expected from work reported by others (1, 13), different carcasses contained different amounts of the three vitamins; the percentage retained after cooking also showed a considerable degree of variability (Table I).

TABLE I

VITAMIN CONTENT OF FRESH PORK AND PERCENTAGE RETAINED AFTER COOKING

(Values represent means of duplicate determinations)

Half-back	Uncooked			Cooked		
	$\mu\text{gm.}/\text{gm. dry wt.}$			Percentage retained		
	Thiamine	Riboflavin	Niacin	Thiamine	Riboflavin	Niacin
1	68.3	5.55	213.3	59.0	76.6	69.9
2	79.0	6.84	258.6	65.0	77.2	71.4
3	52.8	6.48	229.5	75.8	75.5	66.3
4	64.4	5.04	177.7	77.7	86.7	68.8
Mean	66.1	5.98	219.8	69.4	79.0	69.1

Analyses of variance were used to determine whether significant losses of vitamins occurred during the curing process, and whether the percentage retained after cooking was affected. The results are presented in Table II. Curing caused significant losses of thiamine and niacin but caused little change

in riboflavin content. The percentage of all three vitamins retained after cooking was somewhat higher in cured pork than in uncured pork, but the difference was significant for niacin only.

TABLE II

THE EFFECT OF THE CURING PROCESS UPON THE VITAMIN CONTENT OF PORK
AND THE PERCENTAGE RETAINED AFTER COOKING

Treatment	Uncooked			Cooked		
	$\mu\text{gm./gm. dry wt.}$			Percentage retained		
	Thiamine	Riboflavin	Niacin	Thiamine	Riboflavin	Niacin
Uncured ^a	66.1	5.98	219.8	69.4	79.0	69.1
Cured ^b	51.9	5.82	152.0	77.0	86.2	80.9
Necessary difference, 5% level	12.6	—	54.3	—	—	9.3

^aValues represent means of four determinations in duplicate.

^bValues represent means of 16 determinations.

The vitamin contents of samples subjected to various cures did not differ significantly. However, there were significant differences in the percentage of riboflavin and niacin retained after cooking, the highest retentions being associated with low chloride content (Table III).

TABLE III

THE EFFECT OF DIFFERENT CURES UPON THE PERCENTAGE OF THREE VITAMINS RETAINED
AFTER COOKING

(Each value represents the mean of 10 determinations)

Vitamin	Nitrate, 0.2%					Nitrate, 0.1%			Necessary difference, 5% level
	Chloride, %					Chloride, %			
	2	3	4	5	6	2	4	6	
Thiamine	83.7	83.3	78.8	72.1	84.7	82.8	85.1	77.8	—
Riboflavin	94.0	90.2	87.7	80.5	86.9	86.8	92.5	85.5	6.5
Niacin	87.6	89.6	84.7	79.6	81.3	91.0	85.2	84.0	7.5

There was a significant loss of thiamine and riboflavin, but not of niacin, from cured pork stored at 30° F. for 24 days (Table IV). During this period the percentage of thiamine retained after cooking gradually increased until the difference attained statistical significance. No such increase occurred with riboflavin or niacin.

TABLE IV

THE EFFECT OF STORAGE AT 30° F. UPON THE VITAMIN CONTENT OF CURED PORK AND THE PERCENTAGE RETAINED AFTER COOKING

(Each value represents the mean of 16 determinations)

Vitamin	Storage time, days					Necessary difference, 5% level
	0	6	12	18	24	
	μgm./gm. dry wt.					
Thiamine	51.9	38.9	46.0	41.4	37.8	9.5
Riboflavin	5.82	5.31	5.39	5.64	4.78	0.58
Niacin	152.0	162.4	151.5	164.9	150.4	—
	Percentage retained after cooking					
Thiamine	77.0	78.3	75.3	88.6	85.8	7.5
Riboflavin	86.2	87.8	87.6	87.7	90.8	—
Niacin	80.9	86.2	83.1	88.8	87.7	—

Discussion and Conclusions

The loss of significant amounts of thiamine and niacin during the curing process (Table II) suggests that these two vitamins leach into the pickle, whereas riboflavin does not. After pork hams have been wet-cured and smoked, they have been found to lose more thiamine than niacin or riboflavin (16, 17). It was thought possible that differences in vitamin content between the present materials, subjected to eight different cures, might have been obscured, in part, by occasional failure to attain the desired chloride levels. However, even when the actual chloride contents are considered there is still no well-defined relation between vitamin content and the chloride or nitrate content of the cured pork.

The average vitamin retentions during the storage of pork products, reported by various investigators, are shown in Table V. Rice, Fried, and Hess (14) found that ground flank muscle spoiled after storage for 14 days at 40° F. They attributed subsequent high vitamin retentions to synthesis by spoilage microorganisms. Under approximately comparable conditions of storage, cured half-backs lost somewhat more thiamine than fresh hams, fresh loins, or fresh or cured ground flank muscle; all lost about the same amount of riboflavin; but, unlike fresh hams, fresh loins, or cured ground flank muscle, cured half-backs lost no niacin.

Losses of thiamine, niacin, and riboflavin occur during the cooking of fresh pork (1, 8, 9, 12, 14, 15, 16). These losses increase the more the pork is cooked, with loss of thiamine greatly exceeding losses of the other two vitamins (5). Under the cooking conditions used in these experiments, both in uncured and cured pork, the percentages of thiamine and niacin retained were about

TABLE V
RETENTIONS OF THIAMINE, RIBOFLAVIN, AND NIACIN IN STORED PORK PRODUCTS REPORTED
BY VARIOUS INVESTIGATORS

Source of data	Material	Storage conditions		Average retention, %		
		Temp., °F.	Time, days	Thia- mine	Ribo- flavin	Niacin
Schweigert, McIntire, and Elvehjem (16)	Fresh hams	24.8	14	92	85	92
Rice, Fried, and Hess (14)	Fresh loins	40	6	101	93	81
			10	107	100	63
			20	95	90	64
			68	97	94	78
	Ground flank muscle	40	7	95	100	102
			14	93	104	97
			21	95	118	97
			28	87	154	101
	Ground flank muscle, nitrate-nitrite-glucose cured	40	14	95	105	90
			56	91	120	93
Gorham (calculated from Table IV)	Half-backs, sodium chloride-nitrate-nitrite cured	30	6	75	91	106
			12	89	93	100
			18	80	97	108
			24	73	82	99

equal and lower than the percentage of riboflavin retained (Table II). The higher percentage of niacin retained after cooking in cured than in uncured samples may bear some relation to the type of cure since it decreased as the sodium chloride content increased (Table III). Initially, the percentage of thiamine retained after cooking was not significantly affected by curing (Table II), as Greenwood and associates have reported (3), but, during subsequent storage, the thiamine retained after cooking increased to a significant degree (Table IV). There is need for further study of curing as it affects the amount of vitamin retained after cooking. The variability observed in the present study may be reduced by the use of a more rigidly standardized cooking procedure.

These experiments, conducted on a semicommercial scale, indicate that an appreciable loss of thiamine, riboflavin, and niacin occurs during the curing of pork in fresh brine pickle and its subsequent storage at 30° F. In commercial practice, however, where many whole backs are cured in brine that is used repeatedly, the losses may not be as great.

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APPARATUS FOR MEASURING OXYGEN CONSUMPTION OF GUINEA PIGS¹

BY FLORENCE A. FARMER² AND E. W. CRAMPTON³

Abstract

A modification of the Teitelbaum and Harne apparatus for measuring oxygen consumption in guinea pigs has been described. Typical results are given to illustrate the usefulness of the apparatus.

Many types of apparatus have been used to record the oxygen consumption or carbon dioxide production, or both, of animals, as an indirect method for determining their metabolic rate.

The apparatus to be described in this paper (Fig. 1) is a modification of the one designed by Teitelbaum and Harne (1) in which water is drawn into a burette to replace oxygen consumed by the animal.

In any apparatus used for measuring oxygen consumption, a chamber is needed that can be easily opened to admit the animal, readily made airtight again, and conveniently cleaned between each test run. A 10-in. desiccator has proved satisfactory for this purpose. The soda lime is held around the side wall of the desiccator in a removable two-walled container of screening, which rests on a perforated floor. The desiccator can thus be cleaned after each run, without necessarily changing the soda lime. The desiccator is sealed with high vacuum stopcock grease. Lanoline works well but is objectionably sticky. Vaseline cannot be used.

Since it is possible to watch the activity of the animal through the glass top, the respiration rate can be counted while the test is in progress.

The graduated dispensing burette is simple to operate since the level of water can be read off directly and then the burette emptied ready for the next run, without disturbing its position.

Water is maintained in the siphon at all times, regardless of changes in pressure within the burette, by means of the test tube and constant leveling device.

Results

This apparatus has been in continuous use in this laboratory for eight months during which time approximately 500 tests have been run on 50 animals. Some typical results are recorded below.

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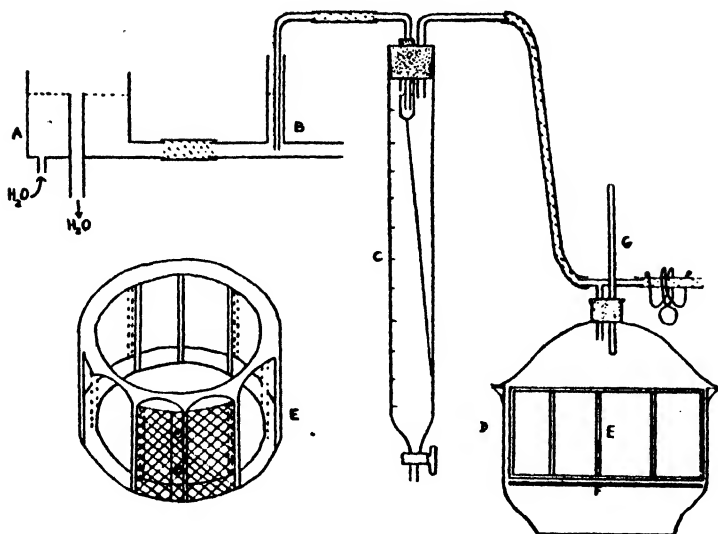


FIG. 1. *Apparatus for measuring oxygen consumption of guinea pigs.*

A. A water leveling device made of chromium plated brass.

B. A 'T' tube joined to A by rubber tubing. There are four in the series, each unit capable of working alone or with the others.

C. A 1000 cc. dispensing burette fitted with a rubber stopper. Hung from the stopper is a test tube with a hole in it. The glass tubing (siphon from B) is below the level of the hole, so that the siphon can be maintained. The height of the burette is adjusted until the hole is at the level of the water in the 'T' tube (B). Thus no water flows into the burette unless the air pressure is reduced. The string hanging from the test tube prevents splashing.

D. A desiccator fitted with a rubber stopper. A 'T' tube not only allows air to pass from the burette C into D, as the pressure in D drops, but also permits the operator to suck the air out of D to start the siphon from B to C at the beginning of the test.

E. A two-walled wire basket holding soda lime. A frame of brass (chromium plated) is made of two disks held together by rods. The inner screening is threaded between the two sets of rods and secured permanently. The outer screening (copper) surrounds the outer rods and is fastened with two snaps. It can be removed to change the soda lime. The top disk is cut away between each set of rods, to allow for filling the basket by means of a spoon.

F. A perforated floor (chromium plated brass).

G. A thermometer.

To run the test

1. Turn on the water until the level is constant in B.
2. Suck on 'T' tube in D until the water rises in B and siphons over into the test tube in C. Continue sucking until water reaches some mark in C to be used as starting level.
3. Remove lid from desiccator and put guinea pig in. Replace lid and seal. Seal all other joints with stopcock grease if necessary.
4. Seal off the 'T' tube in D with a pinchcock.
5. The test is continued until a given amount of water (300 cc. or 500 cc.) has been drawn over.

Caution

All connections must be airtight.

Uniformity of Response

Table I shows the oxygen consumption of a guinea pig determined daily for 15 days. As would be expected, the day to day variability decreases as the animal becomes accustomed to the apparatus.

TABLE I
OXYGEN CONSUMPTION ON SUCCESSIVE DAYS

Date	Oxygen, ml./min.	Date	Oxygen, ml./min.
Jan. 25	8.8	Feb. 4	10.7
26	10.1	5	10.4
27	9.8	6	11.5
28	11.1	7	10.5
29	8.8	8	10.3
31	9.9	10	10.8
Feb. 1	10.6	11	10.6
3	11.5		

Oxygen Versus Air

The test can be run until such time as the oxygen of the air in the apparatus has been used up. There is no advantage in using pure oxygen in place of air. This is shown by the fact that a pregnant guinea pig drew over water equivalent to 13.7 ml. per min. when air filled the apparatus and 14.6 ml. per min. when pure oxygen was used three days later.

Our data indicate that unless the difference between single runs exceeds 15%, the probability ($P = 0.05$) is that the tests are not really different.

Exhaustion of Soda Lime

The rate at which carbon dioxide is absorbed on the soda lime depends upon the concentration of carbon dioxide in the apparatus and the quantity of soda lime present. Indicator soda lime (450 gm.) is used in each desiccator. Since some animals produce carbon dioxide at a greater rate than others, all tests have been run until a fixed amount of water (300 ml.) has been drawn over, rather than for a fixed time. In this way, the concentration of carbon dioxide at the end of the run is always the same. Our results show that soda lime can be used until it begins to turn blue. Under the conditions of our procedure, each pound of soda lime will absorb carbon dioxide equivalent to 10 liters of water.

Fasting of Animals Prior to Test

We have not made extensive tests comparing basal with resting metabolism. Because of the fasting necessary, and its effect on live weight changes in animals subjected to repeated tests at weekly intervals, basal metabolism could not be employed in the studies for which this apparatus was designed. However, as a matter of interest a few runs were made to determine the effect of fasting on the variability of the oxygen consumption records.

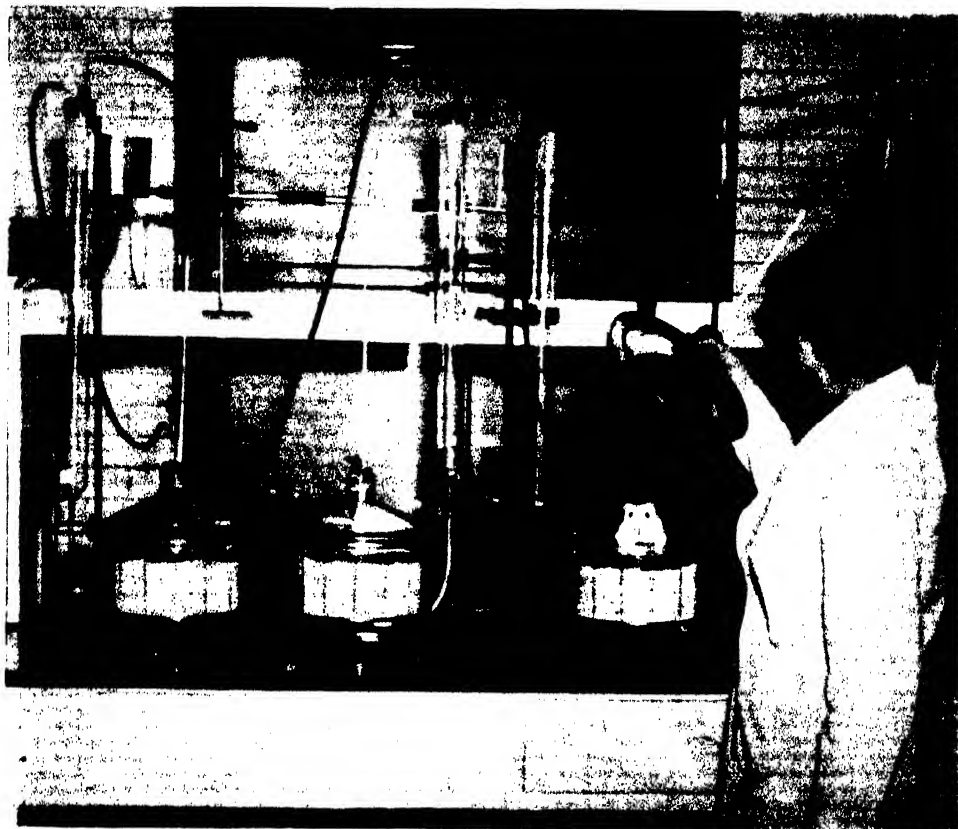


FIG. 2. Showing actual assembly of apparatus for measuring oxygen consumption of guinea pigs.

The guinea pigs used for this work were pregnant and on ad libitum feeding. The oxygen consumption of three non-fasted animals was determined on three alternate days. These animals showed a mean oxygen intake of 12.3 ml. per min. and a coefficient of variation of 7.8%. The experiment was then repeated on the same animals, with a 21-hr. fast before each run. This time the average oxygen consumption was lower (10.4 ml. per min.), as would be expected, and the coefficient of variation was 6.2%.

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THE REDUCING SUGAR CONTENT OF FROZEN EGG AS AN INDEX OF THE BACTERIAL CONTENT¹

By C. K. JOHNS²

Abstract

Reducing sugar determinations have been proposed as an over-all measure of both bacteriological and chemical changes in frozen egg. When applied to commercial products, the technique recommended has been found to yield poorly reproducible results, while reducing sugar readings show no correlation with viable or microscopic counts of bacteria. Few of the bacteria isolated from commercial melange were able to ferment glucose.

In assessing the quality of frozen egg, the bacterial content deserves consideration, since a high count usually denotes either low grade breaking stock or faulty plant operations. Furthermore, a high count product may spoil during defrosting, while conditions that allow considerable bacterial growth may permit the multiplication of pathogenic types, with a consequent possible public health hazard (2, 3, 4, 7, 10, 11, 12).

However, quality in frozen egg includes other aspects in addition to the bacterial. The type of breaking stock, or the growth of bacteria in the melange, may be reflected in chemical changes, some of which give rise to undesirable flavors and odors in the product. Consequently, various chemical tests have been suggested (6). Among these is the determination of the reducing sugar content. This test has recently been advocated as an over-all indication of egg quality by Pearce and Reid (8), who report that reducing sugar values decreased with increasing numbers of bacteria. Such a test, giving promise of indicating both chemical and bacteriological aspects of egg quality, would be extremely useful in the regulatory control of frozen egg.

It is generally recognized, however, that the bacterial content of a food product has to be well up in the millions per gram before the effect of bacterial activity can be measured by ordinary chemical tests. Consequently, there was reason to doubt the effectiveness of the reducing sugar test as a means of measuring or reflecting the bacterial content. With this in mind, studies were undertaken to determine the degree of correlation between bacterial content and reducing sugar content of commercial frozen egg, and also between each of these measures and plant conditions and operations as observed at the time of sampling. However, since only a few plants were operating when the frozen material was sampled, such observations were obviously of limited value.

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Materials and Methods

During October and November, 1946, Mr. D. A. Fletcher of the Poultry Products Marketing Service, Department of Agriculture, visited a number of plants between Ottawa and the Pacific coast where eggs were broken and frozen for the domestic trade. At each plant, cores of whole egg, white, and yolk were bored, using a sterile 1 in. corer and an electric drill. One portion of the core was placed in a sterile stoppered 7/8 in. \times 6 in. Pyrex test tube and kept frozen. When all samples from any city had been collected, they were carefully packed in dry ice and shipped by air express to Ottawa. Here they were rapidly thawed in a water bath and analyzed for (a) total viable count on standard milk agar at 32° C. for three days, (b) direct microscopic count, and (c) coliform count on Bacto violet red bile agar at 37° C. (1). A second portion of each sample was analyzed by Mr. Fletcher in the field for reducing sugars and total solids, using for the former the method employed by Pearce and Reid (8). An additional determination of reducing sugar was made by the Division of Chemistry, Science Service, on the portion of sample remaining after bacteriological analysis, in order to establish reproducibility of results between two workers using the same reagents, etc.

Results

Fig. 1 shows data obtained from 59 samples of frozen whole egg. The lack of correlation is obvious. The majority of samples with viable counts below 1,000,000 per ml. were below the minimum of 300 mgm. %* reducing sugar that had been suggested for Grade A whole egg, while a number of those with very high counts were well above this limit.

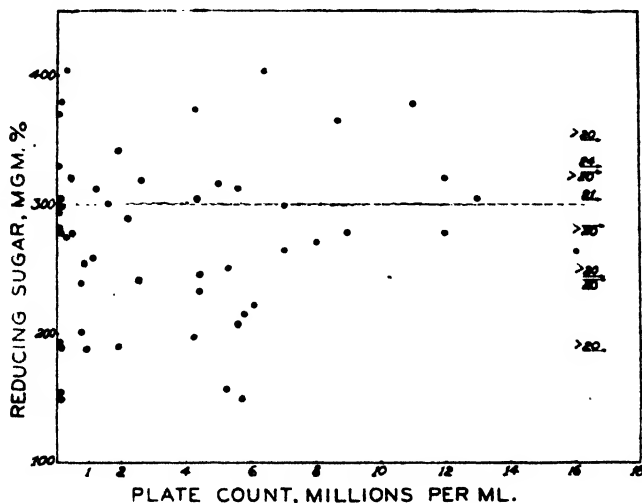


FIG. 1. Reducing sugar content vs. plate count of 59 samples of commercial frozen whole egg.

*This represents the number of milligrams in 100 gm., or the percentage $\times 1000$.

Fig. 2 shows similar data obtained from frozen yolk and white. Again, the lack of correlation is obvious.

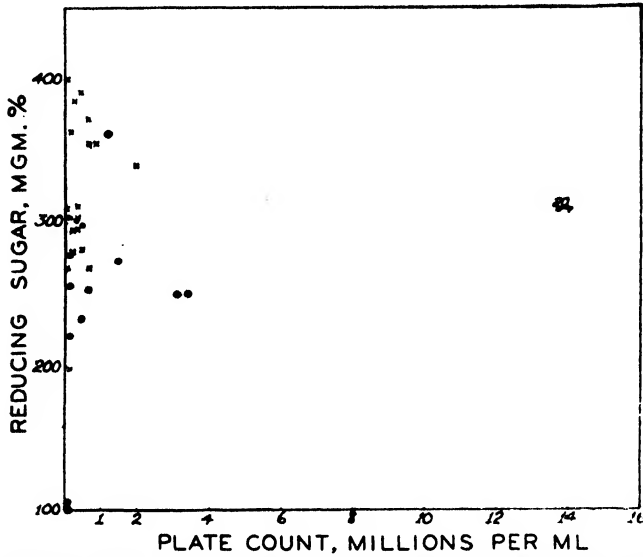


FIG. 2. Reducing sugar content vs. plate count of commercial frozen yolk (14 samples) and white (20 samples). ● = yolk; × = white.

In Figs. 1 and 2 the reducing sugar values are those determined by Mr. Fletcher. The poor agreement between these values and those obtained by the Division of Chemistry is evident from the data in Fig. 3. In general,

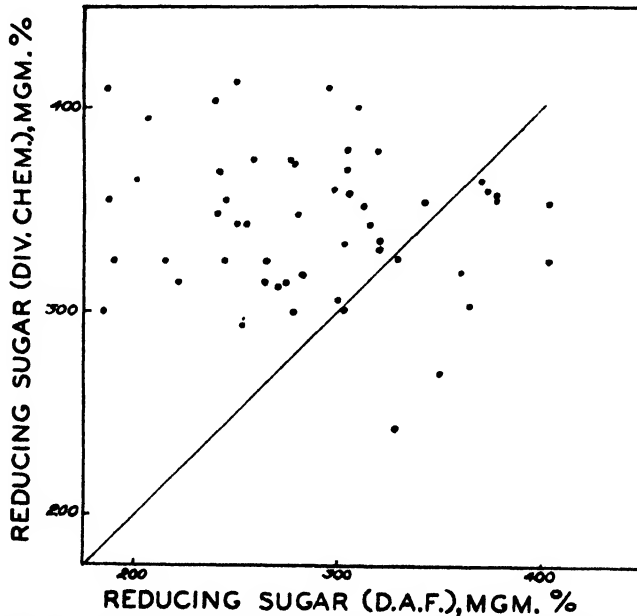


FIG. 3. Reducing sugar contents of 53 samples of commercial whole egg as determined by two different workers.

each of the two analysts obtained reasonably satisfactory agreement between their own duplicate determinations. However, subsequent studies, in which the same two workers made parallel determinations in the same laboratory, failed to yield results in close enough agreement to warrant the use of this test in its present form.

The results of an attempt to relate plant conditions and practices to reducing sugar and bacterial contents appear in Table 1. While the reducing sugar

TABLE I

RELATION BETWEEN QUALITY OF BREAKING STOCK, PLANT CONDITIONS AND PRACTICES, ETC., AND BACTERIOLOGICAL AND CHEMICAL DATA

Sample No.	Reducing sugars, mgm. %		Viable count per ml.	Microscopic count per ml.	Coliform count per ml.
	D.A.F.	Div. Chem.			
<i>A. Eggs broken and frozen under ideal conditions</i>					
31	370	364	75,000	—	<100
32	342	353	1,900,000	5,600,000	<100
93	403	330	6,400,000	3,700,000	51,000
94	377	355	11,000,000	3,200,000	30,000
<i>B. Melange produced under sanitary conditions but lacking facilities for fast freezing</i>					
86	222	315	6,000,000	7,900,000	400
87	215	325	5,800,000	9,200,000	<100
88	258	375	1,100,000	3,200,000	78,000
89	239	403	760,000	1,800,000	13,000
90	207	395	5,600,000	6,300,000	38,000
91	193	465	60,000	—	14,000
92	190	325	1,900,000	5,300,000	56,000
<i>C. Melange from candling bench mixed eggs</i>					
1. Placed in good freezer fairly promptly					
70	364	302	8,700,000	12,000,000	400
71	403	354	300,000	3,300,000	<100
74	350	271	>20,000,000	33,000,000	<100
75	298	360	7,000,000	20,000,000	200
2. Placed in poor freezer at end of each day's operations					
54	244	325	>20,000,000	>33,000,000	>100,000
55	242	368	20,000,000	33,000,000	10,000
62	250	—	3,100,000	5,100,000	100
63	273	378	1,500,000	1,900,000	<100

values as determined by Mr. Fletcher appear to correlate well with plant practices and conditions, an inverse relationship exists when the Division of Chemistry values are used. Bacterial counts appear to show little or no

correlation with plant practices. However, it should be pointed out that in most plants such important points as adequacy of sanitizing of utensils and equipment could not be checked, since the sampling was conducted many months after breaking operations had ended.

Discussion

The lack of correlation between bacterial numbers and reducing sugar content found in these studies is not altogether surprising. Even if a close correlation existed between the reducing sugar content and the bacterial content of the egg at the moment of breaking, this might easily be upset by a heavy pick-up of bacteria from equipment. If no opportunity existed for subsequent bacterial growth in the melange before freezing, this would not affect the reducing sugar content. Furthermore, various workers have shown that a high proportion of the bacteria present within the egg are unable to utilize reducing sugars in their growth processes. Finally, there is little published information concerning the effect of climate, season, storage, and other factors upon the reducing sugar content, and little is known as to how widely normal eggs vary in this constituent.

The lack of agreement between our results and those reported by Pearce and Reid (8) concerning the correlation between bacterial numbers and reducing sugar content may arise from the fact that they worked with Grade A eggs, broken out under nearly aseptic conditions in the laboratory, while our samples were obtained from a number of commercial plants breaking and freezing lower grades of eggs. It is probable that sugar-fermenting types, coming from the shells, were more common in their melange; Gillespie (5) has noted that Gram-positive cocci make up a very considerable part of the normal flora of the egg shell, while they occur infrequently in commercial melange. This we had also found to be true in previous studies. For further confirmation, plates from five samples of frozen whole egg in the present studies were selected; from each 50 adjacent colonies were fished onto slants of Difco tryptone glucose extract milk agar (1) containing brom-cresol purple indicator. After incubation at room temperature for two to three days, the slants were examined and any evidence of acid formation recorded. Results were as follows:

Sample No.	Reducing sugar, mgm. %		Viable count per ml.	Acid formers, %
	D.A.F.	Div. Chem.		
42	250	343	5,300,000	< 2
45	373	359	4,300,000	2
52	275	314	280,000	12
54	244	325	>20,000,000	< 2
55	242	368	>20,000,000	< 2

With such small proportions of acid-forming bacteria, a high degree of correlation between reducing sugars and bacterial numbers could scarcely be expected.

Although the data are not shown, direct microscopic counts also showed no better correlation with reducing sugar readings than did viable counts. At first it appeared that the content of coliform organisms might afford a good index to the bacteriological and sanitary quality, but analysis of additional samples revealed many anomalies between coliform content, other bacteriological counts, and reducing sugar content.

In 1921, discussing the proposal to use the reducing sugar content, Redfield (9) remarked: "Whether Todd's general deduction (p. 512), that the dextrose content is a more reliable indication of the age of the eggs than the ammonia nitrogen, is true or not depends entirely upon the bacterial flora of the eggs and whether the predominating changes during aging are fermentative, proteolytic, or lipolytic. Since they may be any of these, the quality of eggs cannot be judged by any one chemical method." Our findings appear to underline the last sentence. While it would be most convenient to have a single chemical test that would indicate over-all quality in frozen egg, in view of the considerations indicated by Redfield, it seems unlikely that one will be found. Apparently, it will be necessary to resort to a combination of bacteriological and chemical examinations, supplementing organoleptic tests, in order to obtain a true picture of the quality of frozen egg products.

Acknowledgments

Thanks are extended to those firms that made available for sampling their stocks of frozen eggs; to Mr. D. A. Fletcher of the Poultry Products Marketing Service, for collecting samples and data, and for making available the results of his reducing sugar determinations; to Mr. J. T. Janson and his staff of the Division of Chemistry, Science Service, Department of Agriculture, Ottawa, for making the additional reducing sugar determinations reported; and to Mr. J. G. Desmarais for technical assistance with the bacteriological tests.

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THE RESISTANCE TO WEATHERING OF COTTON DUCK TREATED WITH CERTAIN COMPOUNDS OF IRON, CHROMIUM, AND COPPER¹

BY MURIEL W. WEATHERBURN² AND C. H. BAYLEY²

Abstract

Unbleached cotton tentage duck was impregnated with chromic oxide, copper carbonate, and ferric oxide, both singly and in mixtures, each metal being present in concentration of approximately 1% as metallic oxide, and also in the form of naphthenates in equivalent concentration. The rot resistance of the treated samples was determined by measuring the loss of breaking strength on soil burial after leaching in water and after outdoor weathering for four months. Photochemical degradation on weathering was determined by measuring the loss of breaking strength and increase in cuprammonium fluidity. The decrease in metal content on weathering was also measured.

Samples treated with chromium and iron in inorganic form, used singly and together, showed no resistance to soil burial and very slight resistance when the metals were present as naphthenates. All treatments containing copper produced substantial resistance to soil burial, the mixtures producing greater resistance than the single compounds; the resistance resulting from treatment with chromium plus copper and with chromium plus copper plus iron mixtures was greater than that from the corresponding copper plus iron treatments. On the whole, the inorganic treatments produced more resistance to soil burial after leaching than the organic treatments but, after weathering, the copper alone and copper plus iron treatments produced less resistance than the corresponding naphthenate treatments.

All the inorganic treatments containing chromium exerted a marked protective effect against deterioration resulting from weathering as judged by breaking strength losses and increases in cuprammonium fluidity.

The naphthenate treatments containing chromium and the iron oxide and iron naphthenate treatments afforded some protection with respect to breaking strength loss but produced fluidity increases approximately the same as that of the untreated fabric. Similar results were obtained with the copper carbonate plus iron oxide treatment.

The samples treated with copper carbonate and copper naphthenate showed breaking strength losses approximately the same as that of the untreated control but gave evidence of enhanced degradation as judged by the fluidity data.

Losses of chromium on weathering were negligible in all cases while losses of iron ranged from zero to 34%. Complete loss of copper occurred in the copper carbonate treated sample and a slightly lower loss (85%) in the copper plus iron treated sample. In the presence of chromium and chromium plus iron, the losses of copper were reduced to 34% and 54% respectively. Similar trends were observed with the naphthenate treatments but the losses were much lower in all cases, ranging from no significant loss to a loss of 48%.

Treatments involving the application of chromium, iron, or copper in various inorganic forms have long been used for the protection of cellulosic fabrics from microbiological attack. Thus for example a treatment usually referred to as 'mineral khaki' or 'mineral dye' has been used widely throughout the British Empire for the protection of such fabrics as tentage ducks. In this process the fabric is treated with a solution of chromium and iron salts and the treatment is subsequently 'developed' by passage of the fabric through an

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² Chemist.

alkaline bath containing sodium hydroxide and sodium carbonate, or both, the fabric being subsequently washed with water and dried. The chromium and iron fixed on the fabric in this process are present as hydrated oxide, the metals being in trivalent form. The treatment appears to impart considerable protection against the actinic degradation that normally occurs in cotton fabrics on exposure to outdoor weathering (2, 9, 15) and against similar degradation occurring during accelerated weathering (8). This protection seems to be largely related to the presence of the chromium oxide, which by itself shows a high degree of resistance to weathering (9, 15). Provided that the amount of chromium oxide (Cr_2O_3) does not fall below approximately 0.75% based on the weight of the fabric, the mineral khaki treatment imparts some resistance to mildew, but provides little or no resistance to severe microbiological attack such as occurs through the action of the bacterial flora of normal soil or decaying vegetation under suitable conditions of temperature and humidity (2, 5, 22). In this connection it is of interest to note that a recent Australian report indicates that deterioration of mineral khaki treated cotton tentage duck may result from the accumulation of decaying leaves, etc. on the surface of the fabric. Thaysen and Bunker (26) in summarizing the shortcomings of chromium oxide - iron oxide treatments have stated that such treatments "afford appreciable protection against microbiological decay but cannot claim to ensure permanent protection. Where material is not likely to suffer exposure in soil, in water, or under conditions of excessive dampness, the treatment may be employed until such time as a more effective treatment has been devised."

An interesting modification of the 'mineral dye' process consists in replacing the alkaline developing bath with an aqueous solution of potassium chromate. In this process the chromium is precipitated in the form of a chromium chromate to which the formula $3\text{Cr}_2\text{O}_3 \cdot 4\text{CrO}_3$ has been assigned by Race and co-workers (16). These investigators have shown that chromium in hexavalent form is the only constituent of the chromium-iron treatment that confers rot resistance, and that this chromium chromate is hydrolyzed in the washing process to yield pigments in which the ratio of trivalent to hexavalent chromium increases with time of washing until the hexavalent chromium is completely decomposed. Moreover, these workers have shown that during the washing process some chemical deterioration of the cotton may take place through the action of the chromic acid produced in the hydrolysis. The iron chromate precipitated in the chromate development appears to be more readily hydrolyzed than the corresponding chromium chromate referred to above, and can likewise produce chemical deterioration of the cotton yarn with which it is in contact. Further extensive studies on the properties of the pigments produced by the two types of development and the factors affecting their formation have been made by Race and co-workers (17-21). It has also been found by Race *et al.* (22) that outdoor weathering had a pronounced effect in bringing about hydrolysis of hexavalent chromium.

Data on the behavior of fabrics subjected to iron treatments alone are meagre. Jarrell *et al.* (13) reported that the presence of ferric oxide accelerated chemical degradation occurring during weathering, while Cunliffe *et al.* (8) have stated that such treatments exert a slight protective action toward the effects of weathering. The resistance to microbiological attack afforded by such treatments appears to be negligible.

Copper carbonate treatments have been reported to cause enhanced actinic degradation on weathering and to be readily removed by leaching during weathering (9, 13, 24). Such treatments provide good resistance to microbiological attack for such time as the copper remains in the fabric (6, 10, 11).

The mixture of copper carbonate and iron oxide in cotton yarns and fabrics has been extensively investigated by Race and co-workers who claim that such treatments produce a high degree of resistance to microbiological attack, and also that in such mixtures copper is not as readily removed by water leaching as with the copper carbonate treatment alone. The extent of actinic degradation in several experiments was the same as that of the untreated fabric (2, 5, 15). These data have been challenged by other investigators who claim that the presence of copper in such treatments causes an acceleration of actinic degradation. It was also reported by Race that yarn treated with a mixture of chromium oxide and copper carbonate containing approximately 1% of each metal as oxide showed the same rate of removal of copper by leaching in running water at pH 5.3 to 5.5 as that of yarn treated with copper carbonate alone (23).

In investigating the properties of the copper-iron treatment, Race *et al.* found that incorporation of chromium with the copper and iron salts did not affect the rot resistance as judged by filter candle tests using horse dung inoculum (23). In a copper-chromium-iron treatment the protective value of chromium on weathering was destroyed by the presence of copper (15) although it should be pointed out that the concentration of chromium in this experiment was rather low, 0.39% chromic oxide.

Other work (2) has shown that the after treatment of a typical mineral khaki treated duck with copper naphthenate applied from solvent greatly improved the rot resistance of the mineral khaki treated fabric and did not appear to increase the extent of actinic degradation. Moreover, the loss of copper by leaching during weathering was less than that occurring in a similar fabric treated with copper naphthenate alone.

In view of the conflicting data pertaining to treatments with chromium, copper, and iron referred to above, it was of interest to study the rotproofing efficacy and weathering characteristics of chromium, copper, and iron salts incorporated in cotton duck by alkali precipitation. The metals were used singly, in concentration of approximately 1% expressed as the metallic oxides, and also in binary and ternary mixtures in order to study the interactive effects of the metals in mixture. Investigation was also made of the behavior of these metals when applied to the fabric in similar concentrations from solvent solution in the form of naphthenates.

Materials and Treatments

The cotton fabric was an unbleached army duck weighing 10 oz. per square yard and having 46 three-ply warp and 37 two-ply weft yarns per inch. The chemicals were of technical grade.

All treatments were carried out in the laboratory. The inorganic treatments were applied by a two-bath method in which a loop of fabric was impregnated with a soluble salt of the metal by continuous passage through a laboratory paddler followed by similar passage through a solution of sodium carbonate. A complete description of the method of sampling and treatment by aqueous procedure has been given in a previous paper (2). The concentrations of the treating solutions in the present experiment were as follows:

Bath (1) Chromium impregnation—chromic sulphate

($\text{Cr}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$), 120 gm. per liter

Copper impregnation—copper sulphate

($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$), 50 gm. per liter

Iron impregnation—ferric ammonium sulphate

($\text{Fe}_2(\text{SO}_4)_3(\text{NH}_4)_2\text{SO}_4 \cdot 24\text{H}_2\text{O}$), 67 gm. per liter

For precipitation of mixtures of the compounds, the concentrations of the copper and iron salts were increased to 87 and 93 gm. per liter respectively. Impregnation for 15 min. at 71° C.

Bath (2) Impregnation for 10 min. at 49° C. in a solution of anhydrous sodium carbonate, 50 gm. per liter. The treated fabric was washed for two hours in running tap water.

The naphthenate treatments were applied from solution in Stoddard solvent as previously described (4). The percentage of metal applied in these treatments is expressed in terms of metallic oxides in order to conform with the method of expressing the metallic content of the inorganic treatments.

The colors of the treated fabrics were as follows:

Metal	Inorganic treatments	Naphthenate treatments
Chromium	Medium blue gray	Medium gray with mauve tint
Copper	Medium blue green	Medium blue green
Iron	Medium orange tan	Light tan
Chromium + copper	Medium blue green	Medium blue gray
Chromium + iron	Grayish tan	Medium tan with mauve tint
Copper + iron	Deep tan	Medium grayish green
Chromium + copper + iron	Olive green	Dark gray with greenish tint

Test Methods

The sampling procedure was the same as that used previously (2), each breaking strength value being obtained from 10 breaks, using duplicate sets of five breaks each.

For outdoor weathering the samples were attached to frames as described previously (2) and were exposed on the roof of the National Research Laboratories, Ottawa, from May 1 to Aug. 31, 1946, a period of four months.

The methods used for the determination of breaking strength, soil burial, leaching, and cuprammonium fluidity were those given in Schedule 4-GP-2-1944, *Methods of Testing Textiles*, of the Canadian Government Purchasing Standards Committee. Of the metal concentrations, copper when used alone was determined by the ignition method (7); copper and iron together were determined by the method of Race (15); and other metals, used singly and in combination, were determined by the methods of the Textile Institute of Great Britain (25); the two latter methods were used with slight modifications as described previously (2).

Data

Weather Conditions

Data for rainfall and hours of sunshine during the exposure period are given in Table I. The total hours of sunshine were similar to those during the 1944 (1) and 1945 (2) exposures, and the amount of rainfall was approximately the same as for the 1945 exposure but greater than the 1944 exposure. None of the weathered samples showed evidence of significant mildew growth.

TABLE I
WEATHER CONDITIONS DURING EXPOSURE OF SAMPLES

Period	Mean daily temp., °F.		Rainfall, in.	Bright sunshine, total hours
	Maximum	Minimum		
May 1 to May 4	57	37	0.20	49.5
5 11	57	37	0.54	40.1
12 18	65	44	1.55	51.3
19 25	66	48	0.38	40.4
26 to June 1	68	47	0.23	54.6
June 2 to June 8	71	48	0.71	36.6
9 15	68	46	0.61	78.3
16 22	74	51	3.49	62.3
23 29	91	62	0	83.7
30 to July 6	81	62	0.37	87.9
July 7 to July 13	80	58	0.88	75.5
14 20	86	55	0.04	71.2
21 27	82	59	1.57	46.3
28 to Aug. 3	86	57	0.44	51.8
Aug. 4 to Aug. 10	91	59	2.25	67.1
11 17	79	62	0.11	46.4
18 24	77	52	1.10	26.5
25 31	77	48	0.44	38.4
Average	77	52		
Total			14.91	1007.9

Breaking Strength Loss

Breaking strength data are given in Table II.

Statistical analysis showed that breaks occurring at the jaws of the machine gave lower and somewhat more erratic values than those occurring at some

TABLE II
EFFECT OF WEATHERING AND BURIAL ON BREAKING STRENGTH

	Breaking strength, lb.						Breaking strength loss, %					
	Orig. leached	Weath. 4 months	Buried for two weeks after		Buried for four weeks after		Weath. 4 months	Buried for two weeks after		Buried for four weeks after		
			Leach. 24 hr.	Weath. 4 months	Leach. 24 hr.	Weath. 4 months		Leach. 24 hr.	Weath. 4 months			
<i>Inorganic treatments</i>												
Chromium	189(7)	139(7)	0	10(9)	0	0	26	100	95	100	100	
Copper	181(10)	89(8)	158(7)	37(8)	48(10)	5(10)	51	13	79	73	97	
Iron	184(8)	132(8)	0	20(10)	0	0	28	100	89	100	100	
Chromium + copper	178(6)	176(10)	187(7)	169(6)	104(10)	142(5)	1	+5	5	42	22	
Chromium + iron	195(6)	161(6)	0	15(9)	0	0	17	100	92	100	100	
Copper + iron	181(6)	128(9)	189(9)	116(6)	133(9)	47(8)	29	+4	36	27	74	
Chromium + copper + iron	190(6)	161(7)	206(8)	164(9)	163(9)	136(5)	15	+8	14	14	28	
<i>Naphthalene treatments</i>												
Chromium	211(9)	127(7)	22(10)	40(10)	13(10)	0	40	89	81	94	100	
Copper	202(9)	99(9)	95(9)	98(8)	19(10)	93(10)	51	53	51	91	54	
Iron	207(9)	123(8)	38(9)	53(8)	14(10)	0	41	82	75	93	100	
Chromium + copper	220(9)	143(10)	132(8)	141(5)	32(10)	128(4)	35	40	36	85	42	
Chromium + iron	217(8)	136(6)	66(8)	52(9)	50(8)	0	37	70	76	77	100	
Copper + iron	211(8)	113(7)	137(10)	111(7)	37(9)	103(8)	46	35	47	82	46	
Chromium + copper + iron	211(9)	152(6)	176(9)	155(7)	74(9)	142(9)	28	17	27	65	33	
Untreated control	183(9)	94(7)	0	24(10)	0	0	49	100	87	100	100	

NOTE: Figures in parentheses represent the number of 'good' breaks on which the average was based, jaw breaks being discarded.

distance from the jaws; consequently the 'jaw breaks' were not included in the breaking strength averages. Subsequently in this paper the accepted breaks will be designated as 'good' breaks.

For statistical significance at the 5% level, on averages of 10 good breaks, the necessary differences are as follows: leached samples 17 lb., weathered samples 10 lb., leached and buried samples 21 lb., weathered and buried samples 16 lb. In those cases in which 10 good breaks were not obtained, owing to jaw breaks, a formula described elsewhere (12) was used to test for the significance of differences between certain samples. The percentage losses of breaking strength, as given in Table II, were based on the strengths of the leached original samples. It should be borne in mind that the breaking strength data obtained in this way may be somewhat misleading unless due regard is given to the fact that the naphthenate solutions caused a marked increase in the strength of the original fabric whereas the aqueous procedures had no effect.

Weathering Effects

After outdoor weathering the strength of the copper carbonate treated sample was the same as that of the untreated sample, whereas the strengths of all the other inorganic treated samples were considerably higher than the untreated. Of this latter group the strengths of the samples containing iron alone and copper plus iron were similar, and were less than the strengths of the samples containing chromium plus copper, chromium plus iron, and chromium plus copper plus iron.

Similar relations between the breaking strengths were shown by the samples treated with metallic naphthenates. In this set the difference between the strength of the copper-iron treated sample (113 lb.) and the copper treated sample (99 lb.) is not as great as with the inorganic treatments, but nevertheless the difference is significant since the necessary difference from calculation was found to be 10.7 lb.

Comparing the inorganic and the naphthenate applications, it is apparent that the samples containing copper alone, iron alone, and chromium plus copper plus iron were similar in strength but in all other cases the inorganic treated samples were stronger than the corresponding naphthenate treated samples.

Burial Effects

All samples containing copper showed considerable resistance to burial for two weeks with preliminary leaching, the resistance provided by the copper naphthenate used alone being lower than that provided by the other copper treatments, and the resistance of the naphthenate treatments containing copper being lower than that of the corresponding inorganic treatments. Inorganic treatments of iron and chromium used singly or in combination offered no resistance to soil burial whereas the corresponding naphthenates offered some slight resistance. The superiority of the inorganic mixtures containing copper over the naphthenates was more noticeable after burial for

four weeks with preliminary leaching, although the strength of the sample treated with copper carbonate alone was reduced considerably. The inorganic treatments containing copper plus iron and copper plus chromium were somewhat less effective than the ternary combination, although both of these treatments were more effective than the ternary combination of naphthenates after burial for four weeks. The most effective treatment in soil burial tests was the inorganic combination of chromium plus copper plus iron.

Weathering Followed by Burial

Burial for two weeks after outdoor weathering produced a substantial loss of strength beyond that produced by weathering alone in the case of the chromium and iron treatments, used singly and in combination, both in inorganic and in naphthenate form, and in the case of the copper carbonate used singly. With all other treatments, i.e., copper naphthenate used singly and all binary and ternary mixtures containing copper, there was no significant change of strength on burial for two weeks after weathering. Four weeks' burial caused a substantial decrease in the strength of the fabric treated with copper plus iron inorganic treatment and a slight decrease in the strength of the fabric treated with copper plus chromium and copper plus chromium plus iron inorganic treatment, but did not affect appreciably the strengths of samples treated with copper-containing naphthenate.

Loss of Metal

The data in Table III show that chromium in inorganic form and in the

TABLE III
LOSS OF TREATING COMPOUND ON WEATHERING

	Metal, % ^a						Loss of metal, %		
	Original			Weathered					
	Chromium	Copper	Iron	Chromium	Copper	Iron	Chromium	Copper	Iron
<i>Inorganic treatments</i>									
Chromium	0.98			0.96			2.0		
Copper		0.89			0			100	
Iron			1.23			1.23			0
Chromium + copper	1.00	0.97		0.93	0.64		7.0	34.0	
Chromium + iron	1.00		0.80	0.93		0.66	7.0		17.5
Copper + iron		1.03	1.11		0.15	0.99		85.4	1.1
Chromium + copper + iron	0.72	0.96	0.97	0.69	0.44	0.64	4.2	54.2	34.0
<i>Naphthenate treatments</i>									
Chromium	0.91			0.93			+2.2		
Copper		0.86			0.45			47.7	
Iron			0.90			0.89			1.1
Chromium + copper	0.89	0.90		0.93	0.80		+4.5	1.1	
Chromium + iron	0.80		1.05	0.86		0.82	+7.5		21.9
Copper + iron		0.89	0.88		0.56	0.93		37.1	+5.7
Chromium + copper + iron	0.77	0.92	1.26	0.82	0.87	0.89	+6.5	5.4	29.4

^a Expressed as Cr_2O_3 , Fe_2O_3 , and CuO respectively.

form of naphthenate, both alone and in mixtures, imparted a high degree of resistance to weathering. Iron alone and with copper, both in inorganic form and in the form of naphthenate, imparted a high degree of resistance to weathering but was removed to a moderate extent from the fabrics treated with chromium plus iron plus copper and to a lesser extent from those treated with chromium plus iron. Copper carbonate used alone was completely removed by weathering, and when used with iron oxide produced slight resistance, the loss of copper being 85.4%. The fabrics treated with chromium plus copper and chromium plus iron plus copper inorganic treatment were markedly more resistant to loss of copper. In the naphthenate treated fabrics the copper losses showed the same general trend as in those treated with inorganic copper, but the losses were much less severe.

Cuprammonium Fluidity

None of the treating procedures caused any chemical degradation of the original fabric, as shown by the cuprammonium fluidity data in Table IV.

TABLE IV
EFFECT OF WEATHERING ON CUPRAMMONIUM FLUIDITY

	Cuprammonium fluidity (reciprocal poises)		
	Original	Weathered	Increase on weathering
<i>Inorganic treatments</i>			
Chromium	3.6	10.7	7.1
Copper	3.5	23.4	19.9
Iron	2.9	15.1	12.2
Chromium + copper	2.2	7.7	5.5
Chromium + iron	2.4	7.4	5.0
Copper + iron	3.0	16.1	13.1
Chromium + copper + iron	2.8	9.1	6.3
<i>Naphthenate treatments</i>			
Chromium	3.3	18.9	15.6
Copper	2.8	21.8	19.0
Iron	2.8	17.4	14.6
Chromium + copper	3.4	17.2	13.8
Chromium + iron	2.6	14.9	12.3
Copper + iron	3.0	21.9	18.9
Chromium + copper + iron	3.0	16.8	13.8
Untreated control	3.1	16.9	13.8

With the inorganic treatments, the presence of chromium seemed to give considerable protection against actinic degradation, the fluidity increases of all samples containing chromium being lower than that of the untreated control. The samples subjected to naphthenate treatments containing chromium showed fluidity increases approximately the same as that of the untreated

control. Copper carbonate used alone, and the naphthenates of copper used alone and copper plus iron, produced fluidity increases that were greater than that of the untreated fabric. Samples treated with iron oxide, iron naphthenate, and iron oxide plus copper carbonate showed fluidity increases similar to that of the untreated fabric.

Discussion of Data

These data have confirmed the findings of other investigators and the results of previous work carried out in these laboratories with respect to the properties of treatment with chromium oxide applied singly and in combination with iron oxide. These treatments have been shown to have good permanence to weathering and to provide marked protection against actinic degradation but to impart no resistance to microbiological attack of the type produced by soil organisms. Iron oxide was found to have a considerable degree of permanence but to be without any effect on actinic degradation and to provide no resistance to microbiological attack.

The data also confirm previous observations that copper in the form of copper carbonate, while effective as a rotproofing agent, is readily removed by weathering and tends to increase the extent of actinic degradation.

The addition of iron oxide to the copper carbonate increased the rot resistance and decreased the photochemical degradation produced by the copper carbonate, although the loss of copper on weathering was only slightly lower than the loss from copper carbonate alone. The breaking strength of the fabric containing inorganic copper-iron was slightly greater than, and the rise in its fluidity the same as, that of the untreated fabric.

The addition of chromium oxide to copper carbonate resulted in excellent protection against actinic degradation, as judged by both breaking strength and cuprammonium fluidity, with a substantial reduction of the loss of copper on weathering, as well as a marked improvement in resistance to soil burial. The addition of iron oxide did not affect appreciably the chromium oxide-copper carbonate treatment.

With regard to the naphthenate treatments, it is apparent that chromium and iron possess a high degree of permanence on weathering and impart very considerable resistance to actinic degradation as judged by breaking strength data, but that the resistance as judged by increase in cuprammonium fluidity is much lower than that of the inorganic applications. On the other hand, in naphthenate form, chromium and iron imparted some slight resistance to rotting, whereas in inorganic form they did not produce any measurable resistance. It has been established (8, *) that naphthenic acids impart some rot resistance and it seems possible that these acids might also be responsible for some chemical degradation on exposure to weather. This latter factor is receiving further investigation.

* *Unpublished data, N.R.C.*

Copper naphthenate treated samples showed similar weathering effects to those treated with copper carbonate although the loss of copper was less severe. The lower loss of copper on weathering was probably responsible for the greater resistance of the copper naphthenate treated sample to soil burial after weathering, since the resistance to soil burial after leaching was less than that of the copper carbonate.

The addition of the naphthenates of chromium, iron, or chromium plus iron to copper naphthenate produced effects similar to those of the inorganic treatments, with the exception that the change of cuprammonium fluidity was less pronounced, the increase in fluidity in no case being lower than that of the untreated fabric.

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THE OXIDATION, IGNITION, AND DETONATION OF FUEL VAPORS AND GASES

II. THE EFFECT OF FLOW CONFIGURATION ON THE VELOCITY OF THE OXIDATION REACTION IN PENTANE-AIR MIXTURES¹

BY R. O. KING²

Abstract

Reynolds Numbers for the commonly used rates of flow of a reacting mixture through a conventional combustion tube are far below the critical value. The laminar flow to be expected accordingly is disturbed by convection currents when the tube is heated and flow configuration depends on such factors as ratio of length to diameter and temperature gradients but can be varied by creating local differences of flow velocity within a uniformly heated reaction space such as reaction chamber No. 10 described in Part I. The effects on reaction velocity of the factors mentioned have been determined by experiments described in this part. The results indicate that the velocity of a heterogeneous reaction is determined by flow configuration, that 'packing' does not distinguish between homogeneous and heterogeneous reactions and that the oxidation of pentane, taken as a typical hydrocarbon, is a heterogeneous reaction.

Section I

INTRODUCTION

It was shown by experiments described in Part I (2) that the dimensions and design of reaction spaces were major factors affecting reaction velocity. These factors determine flow configuration and can be varied to produce laminar or turbulent flow or a mixture of both types.

When gas flow through a tube is laminar, velocity is regarded as zero in the layer adjacent to the surface and as increasing in successive layers to a maximum at the longitudinal axis. The average velocity is directly proportional to pressure difference and the energy required to maintain the flow is expended in overcoming viscosity. Laminar flow breaks down to turbulent motion when the velocity through the tube reaches the critical value of the Reynolds Number. Turbulent motion tends to fill the tube and velocity becomes nearly uniform over a cross section normal to the longitudinal axis and is proportional to the square root of pressure difference. The energy required to maintain the flow increases accordingly and is expended in large part in overcoming friction between the wall and the gas stream. The friction gives rise necessarily to a scouring effect.

The flow configuration in an unheated combustion tube can now be considered. A glass tube 2.31 cm. internal diameter was used for many oxidation experiments, air being supplied at the rate of 100 cc. per min. The average velocity is then 0.4 cm. per sec. and the Reynolds Number 6.58. The critical value for ordinary glass tubing is about 2300 in any self-consistent system of units, thus it would be necessary to increase the air supply in the ratio

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2300/6.58, that is, to about 3500 cc. per min. to initiate what is generally described as turbulence. It would be difficult though not impossible to arrange an oxidation experiment accordingly. Alternatively, a local effect on flow configuration equivalent to that obtained when the Reynolds Number exceeds the critical value can be obtained by methods described in succeeding sections.

The flow method of oxidation and mixtures of pentane in combining proportions with air, with one exception, were used for the experiments. The 'pentane' was similar to that used for the experiments of Part I and has been described in the appendix to that part. The experimental results for oxidations are given by graphs, moles of oxygen reacted being plotted against temperature. Methods of measuring air and pentane supply and of analyzing oxidation products were as described in the appendix to Part I.

Section II

FLOW CONFIGURATION AND RELATED REACTION VELOCITY IN NARROW (PACKED) SPACES

The ratio of surface to volume is sometimes increased by packing an open combustion space with fragments of the material of the wall, or with lengths of small tubes of the material if a measurable change in the ratio of surface to volume is required. A sufficiently narrow annulus between two coaxial tubes constitutes a packed combustion space and the arrangement facilitates changes of flow configuration. Tubing of invariable diameter and wall thickness is required for an annulus of uniform width over any considerable length and cannot be obtained in glass except by grinding to size. Recourse was had, therefore, to cold drawn steel tubing, which is of uniform inside and outside diameter, and can be had from stock in great variety of size and gauge. Steel possesses the further advantage that wall temperatures can be measured by the use of thermocouples electrically welded into the tubes at desired positions. Mild steel annular reaction spaces of two designs are illustrated by Fig. 1. Design A provides a straight through annulus and Design B a double annulus with communicating orifices in the partition wall at the position of maximum temperature.

Flow Configuration, Single Annulus

Both tubes were 20 gauge (0.036 in.) wall thickness. The inside diameter of the outer tube was 1.1155 in. and the outside diameter of the inner tube 1.0000 in. The width of the annulus was therefore 0.05775 in. or 1.47 mm. and the area of cross section 1.24 cm². Gas supplied at 100 cc. per min. would pass through the annulus with a velocity of 1.34 cm. per sec., and at the temperature of supply the flow could not be other than laminar. When, however, the tubes are heated in an electric furnace, the outer attains a higher temperature than the inner and if the tubes are vertical the layer of gas adjacent to the outer wall must rise at a somewhat greater velocity than that adjacent to the inner and cooler wall. Relative motion of the two layers becomes greater

than prevails in purely laminar flow and small eddies form between them. The path of the gas being annular in cross section, the eddy motion would be expected to take the form of vortex filaments moving upward with the gas flow.

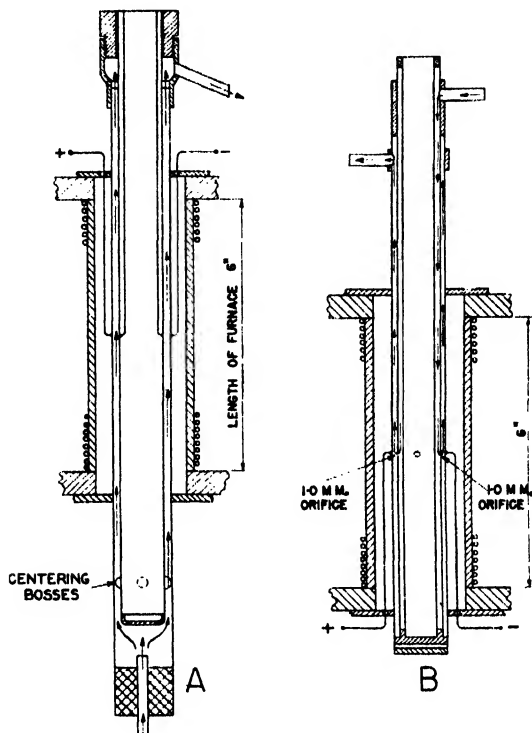


FIG. 1. Annular combustion tubes (steel).

A. Single straight through annulus.

B. Double annulus with four orifices in partition.

Flow Configuration, Double Annulus

The double annular combustion space is so arranged that gas entering the inner annulus at the upper end descends to the position of maximum temperature to pass through four 1.0 mm. orifices, equally spaced around the partition wall, into the outer annulus and thence to the exit at the upper end of the apparatus. The design provides an annular combustion space of the same width as that of Arrangement A and of the same length within the furnace but having means for changing flow configuration at the position of maximum temperature. The flow path of the reacting mixture is otherwise similar to that in the single annulus except for the dead space between the cool end and the ring of orifices. The space might have been filled but after preliminary experiments demonstrated the effect of flow configuration on reaction velocity, it appeared that oxidation in the space would be inappreciable as compared with that in the path of the moving mixture. The area of cross section of the inner annulus was 1.32 cm^2 , that is, only slightly greater than the 1.24 cm^2 .

of the outer annulus; flow velocities would, therefore, be approximately equal. The flow configuration may be taken as similar to that in the single annulus except at the position of maximum temperature where the reacting mixture passes through the four orifices. The total area of cross section of the orifices is 0.031 cm^2 and, that of the annulus being 1.24 cm^2 , gas velocity through the orifices is 40 times greater than the average through the annular spaces. The relatively high velocity creates a purely local disturbance, breaking down the nearly laminar flow and producing a scouring effect over a small surface area.

Preliminary 'Packing' Experiments

Reaction spaces with steel walls are not generally used for laboratory oxidations and the effect of 'packing' was determined by oxidations in the outer tube used alone and in the single annulus of which the same tube forms the outer wall. The inside diameter of the outer tube was 1.1155 in. and, the length within the furnace being taken as reaction space, surface to volume ratio was 1.49. The ratio for the annular reaction space was 13.6 on the same basis. Pentane-air mixtures in combining proportions were supplied at 200 cc. per min. for both experiments. Reaction velocities are given by the graphs of Fig. 2. It will be noted that reaction in the annulus did not begin

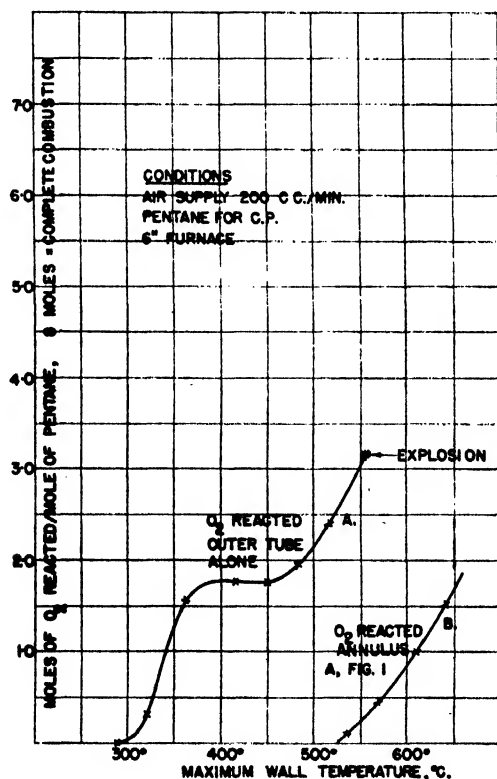


FIG. 2. *Graph A. Reaction rates with convection currents.*
Graph B. Reaction rates with nearly laminar flow.

at a measurable rate until the temperature reached 535°C ., which is beyond the range over which partial oxidation products are usually obtained. The final sample was drawn at 640°C . when the tubes were red hot but explosion did not occur. On the other hand oxygen was reacted at an easily measurable rate in the wide tube at 310°C . The rate increased rapidly over the temperature range 310° to 400°C . giving the familiar hump on the graph associated with profuse formation of aldehyde as described in Part I. The reacting mixture exploded at 560°C . The reaction velocities shown by the graphs of the figure *taken at their face value* show that increase in the ratio of surface to volume leads to a reduction in reaction velocity and support the generally accepted view that reaction chains can be initiated or broken on surfaces. It will be shown, however, by experiments described in succeeding sections that the apparent wall effect to reduce reaction velocity is due to flow configuration, not to the breaking of reaction chains.

Reaction Velocity in the Single Annulus as Affected by Change in Flow Configuration Due to Changing Temperature Difference Between Walls

The single annular combustion tube was set up in a vertical furnace as shown at A, Fig. 1. Pentane-air in combining proportions was admitted at the lower end at the relatively low rate of 40 cc. per min. in order that rates of reaction might be greater than determined for the higher rate of 200 cc. per min. The thermocouples at the position of maximum wall temperature indicated that over the range 400° to 600°C . the temperature of the outer tube was on the average 23°C . higher than that of the inner tube. The difference was 27°C . at 400°C . and 18°C . at 600°C . The average temperature difference was reduced to 20°C . by filling the inner tube loosely with asbestos-magnesia to eliminate convection currents.

Rates for reaction for the two conditions are given by Graphs A and B of Fig. 3. It will be noted that the higher rate of reaction, Graph A, is obtained for the greater temperature difference between the walls although the average temperature is the lower. The 15% increase in temperature difference would increase the *relative* velocity of the ascending layers of gas and consequently the size and velocity of the intermediate vortex filaments and the effect on reaction velocity shown by the graphs is quite remarkable. Thus, at 500°C . outer wall temperature rate of reaction increased from 1.8 to 2.4 moles of oxygen or 33% on increasing the temperature difference between the walls by 15%; at 550°C . the rate of reaction increased by 25%.

Reaction Velocity in the Double Annulus as Affected by Change of Flow Configuration at the Position of Maximum Temperature

The double annular combustion tube shown at B, Fig. 1, was set up horizontally in the 6 in. furnace and a mixture of pentane-air in combining proportions was supplied at 200 cc. per min. The average velocity of gas flow through the annular space was, therefore, 2.7 cm. per sec. and 116 cm. per sec.

through each of the four orifices set at the position of maximum temperature. Velocity ratio remains unchanged on heating. The flow configuration at the position of the communicating orifices is, of course, somewhat speculative but it can be calculated from the width of the outer annulus and orifice diameter that the increased velocity of the reacting mixture flowing through any one of the four orifices at one-quarter of the total rate of supply prevails over a disk 6.7 mm. only in diameter. Thus it may be assumed that the otherwise nearly laminar flow became of a turbulent nature over a relatively small area.

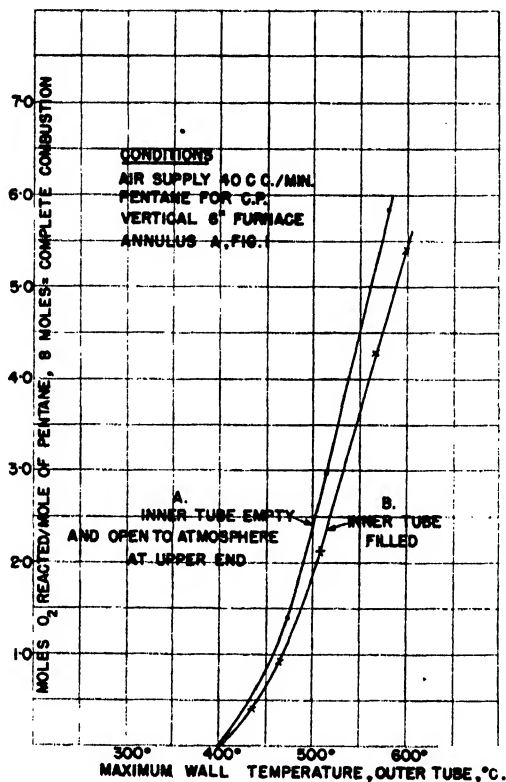


FIG. 3. Change of reaction rate due to small change of temperature difference between walls of Annulus A, Fig. 1.

Reaction rate at temperatures rising to over $600^{\circ}C$. are given by Graph A of Fig. 4 and, for convenient comparison, similar rates obtained for the single annulus in which laminar flow was disturbed by temperature difference only are given by Graph B of the figure, together with rates of formation of carbon oxides.

Referring to Fig. 4, Graph A, it will be noted that, (a) reaction begins at about $125^{\circ}C$. lower than in the single annulus in which flow configuration is nearly laminar, (b) the form of Graph A over the temperature range 400° to $500^{\circ}C$., within which no measurable reaction occurred in the single annulus,

is significant of the formation of partial oxidation products as indicated by the aldehyde hump, (c) at temperatures above the 530°C . at which reaction began in the single annulus, oxidation was mainly to the final products, carbon dioxide and steam; at 575°C . the rate was 630% the greater in the double annulus and at 600°C ., the greater by 560%.

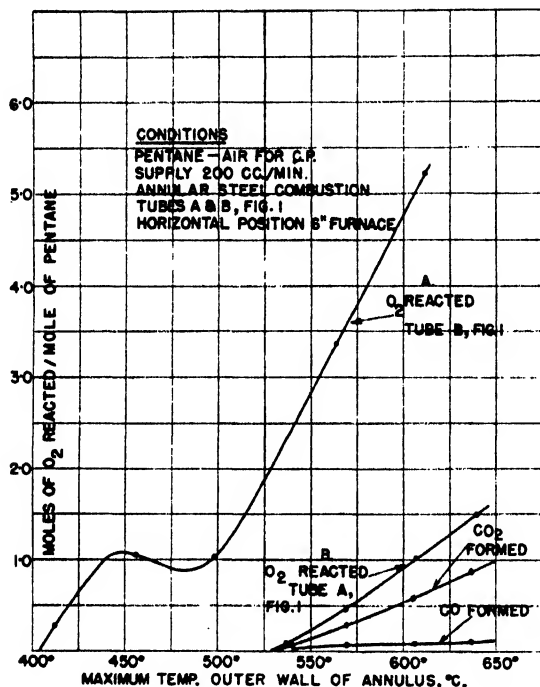


FIG. 4. Effect of local high mixture velocity on reaction in annulus.
Graph A. Mixture passing through orifices, double annulus.
Graph B. Mixture passing straight through single annulus.

Section III

FLOW CONFIGURATION DUE TO HEAT CONVECTION IN UNPACKED COMBUSTION SPACES AND RELATED REACTION VELOCITIES

A useful purpose will be served by discussing the probable flow configuration due to convection currents in an unpacked combustion tube set up vertically in an electric furnace as shown by Fig. 5. When the tube is heated in the usual manner, maximum temperature is reached by a middle part and there are two temperature gradients with a convection circulation over each. The length of the middle part over which there is no temperature gradient depends on the ratio of tube length within the furnace to tube diameter as well as on the width of the space between the inside wall of the furnace and the tube. The figure illustrates the case of a $1\frac{3}{16}$ in. tube supported in a furnace of 2.0 in. internal diameter and 6.0 in. long. The middle part of the tube, of

uniform temperature, does not exceed 1 in. in length and the ratio $\frac{dl}{dt}$ for the temperature gradients increases as the temperature of the middle part is raised. The lower end of the tube contains cold gas being heated while the upper end contains hot gas being cooled so the value of $\frac{dl}{dt}$ is the greater for the lower of the two temperature gradients. When the temperature of the

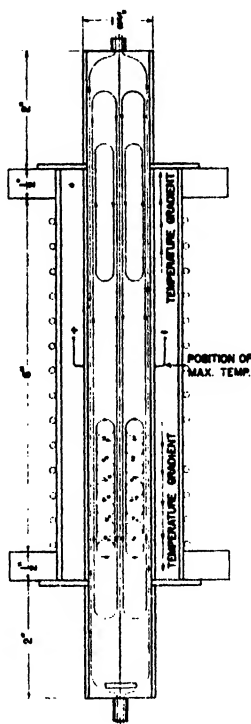


FIG. 5. Possible flow configuration due to convection currents in vertical combustion tube.

middle part of the tube is raised to, say, 600°C . it is reasonable to suppose that cool gas entering at rates of 100 cc. per min. and greater can be raised to that temperature in a tube length of about 3.0 in. solely by repeated contact with the hot walls over the length of the lower temperature gradient. Consequently, the corresponding convection circulation tends to break down into a series of eddies taking the form of rising vortex rings as shown dotted on the diagram. A similar effect would be expected in the upper convection circulation but at the higher maximum temperature required for a suitable value of $\frac{dl}{dt}$. When a 'long' furnace is used and the combustion tube is of relatively small diameter the middle part of the tube attains uniform temperature over a considerable length and convection circulations are set up over the end temperature gradients only, but for tubes of relatively small L/D , as illus-

trated by Fig. 5, the descending stream extends throughout the heated length of the tube. The influence of individual variables on the pattern of the flow configuration would be difficult to determine but assuming that the broad outline is as illustrated by Fig. 5, changes can be effected in various ways and the corresponding reaction velocities measured. This section will be completed by describing a number of related experiments.

Effect of Convection Circulation on the Oxidation of Stainless Steel

A stainless steel (18-8, chromium-nickel) combustion tube $1\frac{1}{4}$ in. internal diameter, set up vertically in a 6 in. furnace was used in earlier experiments to demonstrate the explosion of gaseous combustible mixtures by nuclear drops of water (1). The interior wall of the tube was inspected after hydrogen mixed with air in various concentrations had been passed through it. The rate of supply of the mixture was 200 cc. per min. and maximum wall temperatures varied from 620° to 740° C. The bands of brilliant color seen on the wall were so striking that the tube was split and photographed by infrared light. The photograph is reproduced, Fig. 6. The reddish browns appear as whites and the upper band is overemphasized by glare. It will be noted that oxidation of the steel occurred in the upper and lower parts of the tube. The middle part, at maximum temperature, was coated with blue 'heat scale' and some red that could be seen only by viewing the surface obliquely. Many attempts were made to obtain a greater degree of oxidation of the surface at the middle and hottest position, by changes of hydrogen concentration, but without success. It was supposed at the time of the experiments that the direction of motion of the reacting mixture in the tube was always parallel to the longitudinal axis and, on that assumption, the reason for the formation of oxidation bands *both* top and bottom, *and not at the position of maximum temperature*, remained a mystery. The solution of the 'mystery' is obtained, of course, by abandoning the idea of linear flow, assuming that flow configuration is somewhat as illustrated by Fig. 5 and considering that oxidation of appreciable velocity occurs only at wall surfaces subjected to the scouring action of the eddies accompanying convection circulations.

Direction of Gas Flow and Reaction Velocity

The flow configuration due to convection currents in a combustion tube of relatively large diameter would be expected to differ as between the horizontal and vertical positions and be modified by the direction of gas flow when the tube is in other than the horizontal position. Experiments were made accordingly using a Pyrex tube of 1 in. internal diameter and arranging the gas flow to be vertically upwards or downwards or horizontal. The gas was pentane-air in combining proportions, always passed into the tube at 200 cc. per min. The reaction velocities for the three directions of gas flow are given

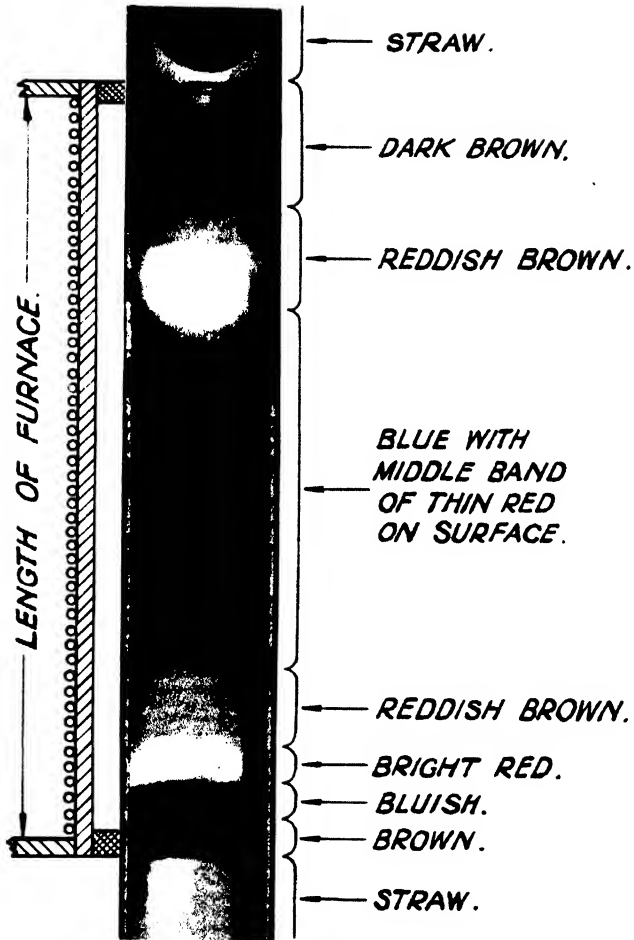


FIG. 6. *Effect of flow configuration on the oxidation of a stainless steel tube.*

by the graphs of Fig. 7. It will be noted that the smallest reaction rate and the lowest explosion temperature were obtained when the gaseous mixture was forced to flow vertically downward. The reaction rate at the temperature of the aldehyde hump increased by 34% on changing the flow from downwards to horizontal and the rate at 550° C. increased by 75% on changing the flow from downwards to upwards.

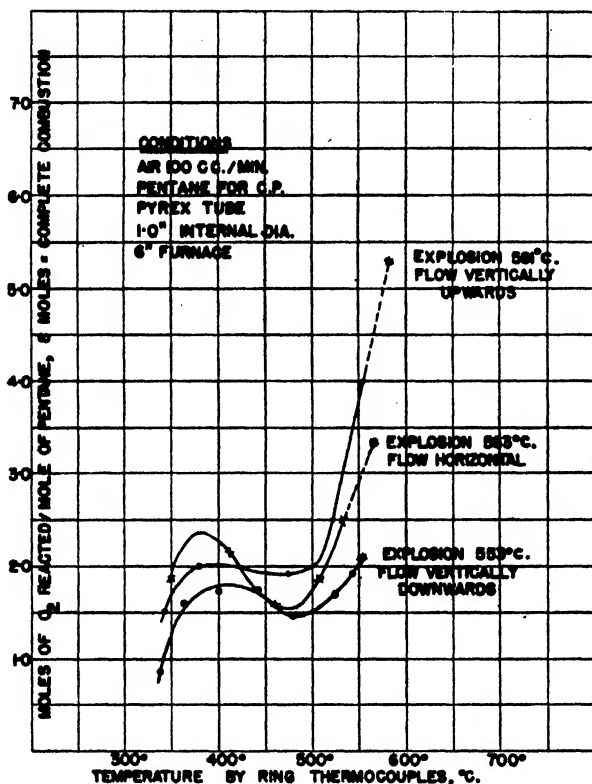


FIG. 7. Effect of direction of mixture flow on reaction rates in Pyrex tube of small L/D .

Effect on Reaction Velocity of Changing Entrance Flow Conditions

The usual method of admitting a combustible gaseous mixture to the cool entrance end of a conventional combustion tube is by a small tube projecting through a cork or rubber stopper as shown at B, Fig. 8. An alternative, generally used in the Cambridge experiments, was the distributor inlet shown at A, Fig. 8. Reaction rates were determined for the two types of inlet, pentane-air in combining proportions being admitted in both cases at 300 cc. per min. The internal diameter of the tube inlet was 6 mm. The velocity of the entering stream was, therefore, 17.7 cm. per sec. as compared with 0.85 cm. per sec. average velocity through the larger tube, and the small stream of relatively high velocity, on reaching the lower convection circulation,

would be opposite in direction to the descending central stream. On the other hand, gas admitted through the distributor inlet enters at the periphery of the combustion tube and rises along the heated walls, the direction of motion coinciding with that of the *ascending* stream of the lower convection

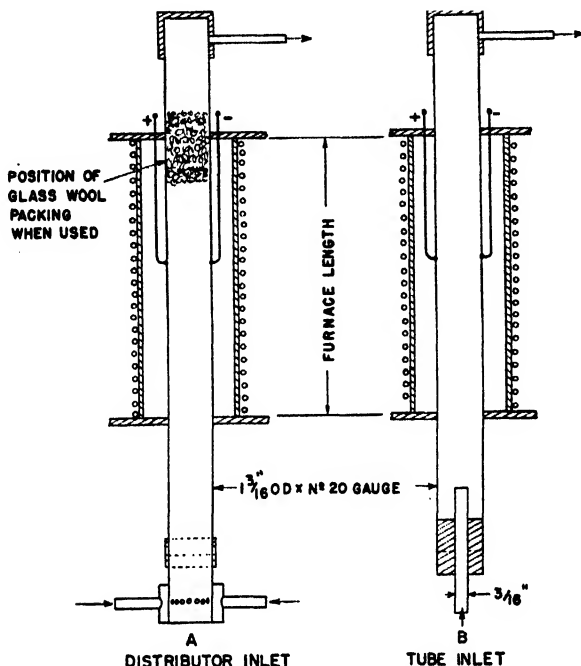


FIG. 8. Mild steel combustion tube with two varieties of gaseous mixture inlet.

circulation. Reaction velocities determined in the two conditions are given by the graphs of Fig. 9 for the temperature range of the aldehyde hump and it will be noted that the rate of oxygen reacted at $450^{\circ}\text{C}.$, when using the tube

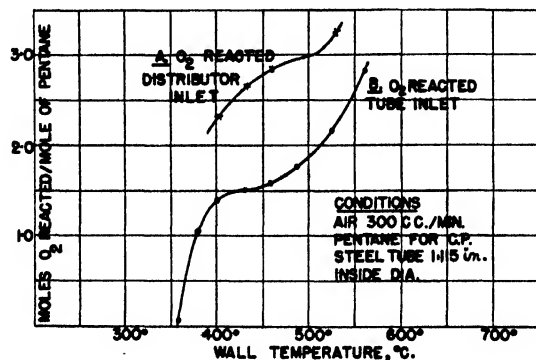


FIG. 9. Effect on reaction rates of change in lower convection circulation due to change of inlet conditions.

inlet, was 1.55 moles as compared with 2.75 moles when the distributor inlet was used. That is, the change in flow configuration due to the use of the distributor inlet accounts for nearly 80% increase in reaction velocity at the temperature mentioned.

Effect on Reaction Velocity of Restricting Upper Convection Circulation

The upper convection circulation in a vertical combustion tube can be restricted to some degree by a plug of loosely packed glass wool, as shown at A, Fig. 8. Reaction rates with and without the packing are given by the graphs of Fig. 10. The distributor inlet was used for both experiments and a

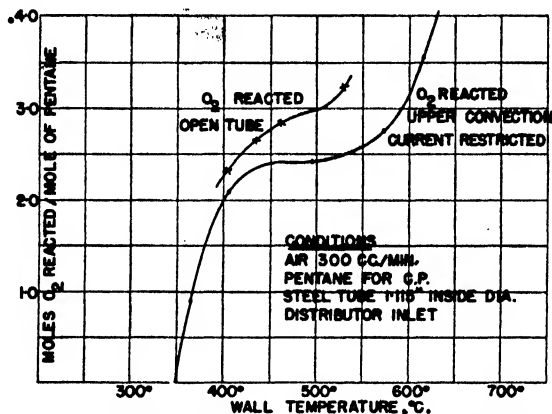


FIG. 10. *Effect on reaction rates of damping upper convection circulation.*

pentane-air mixture in combining proportions admitted at 300 cc. per min. It will be seen by reference to the figure that reaction rate decreased from 3.0 to 2.4 moles of oxygen on restricting the upper convection circulation. The upper circulation is, however, created by the lesser temperature gradient as mentioned earlier and receives partially reacted mixture. Thus, as oxidation of the pentane to aldehyde requires one only of the eight moles of oxygen available, it is probable that reaction accordingly was completed at the position of the lower circulation. The lower reaction velocity at the temperatures of the experiments would, therefore, be expected at the position of the upper convection circulation and change of flow configuration in it would produce less change in the measured over-all reaction rate than if a similar change were made in the lower circulation.

Effect on Reaction Velocity of Changing Flow Configuration in a Single Convection Circulation

The experiments described in preceding paragraphs of this section were made in conditions providing an upper and a lower convection circulation in vertical combustion tubes and 'over-all' reaction velocity only could be determined. The results given below were obtained when using a combustion tube arranged to provide a single circulation extending over the temperature gradient from the middle and hottest part of a vertical combustion tube to the upper end.

The design of the combustion tubes is shown diagrammatically at A and B, Fig. 11. The cool gas of relatively high density admitted at the top of Design A with a velocity of approximately 16 cm. per sec. cannot escape through the outlet without setting up a convection circulation as shown by the diagram.

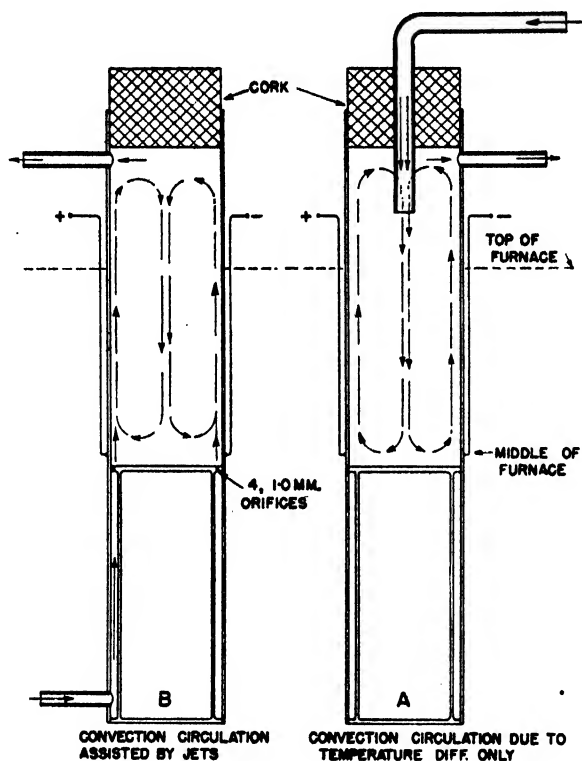


FIG. 11. *Steel reaction chambers in upper half of furnace.*
A. With mixture admitted at relatively low velocity.
B. With mixture admitted by jets assisting convection.

The gas is admitted to Design B at the bottom end and rises through a narrow annulus, in which oxidation is slight, to reach the upper and open space through four 1.0 mm. orifices. The jets issue from the orifices in a position to increase the velocity of the convection circulation already existing by virtue of the temperature gradient but do not impinge on the heated surface of the tube. The odd rate of mixture supply of 167 cc. per min. has no significance.

Reaction velocities determined for the A and B arrangements for pentane-air in combining proportions are given graphically by Fig. 12. It will be seen by reference to Graph A that when flow configuration depended on convection only, the mixture exploded at 600° C. and rate of oxygen reacted never

exceeded 25% of that available. When, however, convection circulation was assisted by the jets, Graph B, reaction was at an extremely high rate but explosion did not occur although the temperature was raised to 660° C. and nearly 95% of the available oxygen reacted accordingly.

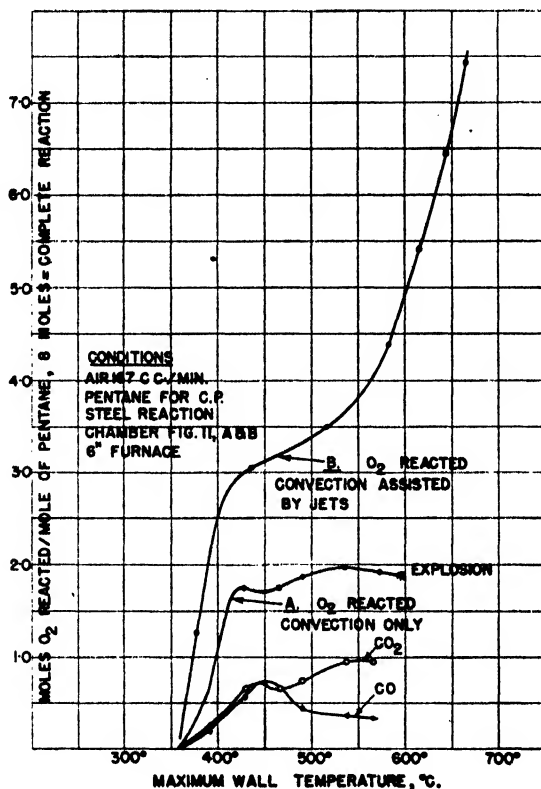


FIG. 12. *Effect of change in convection circulation on reaction rates.*
 Graph A. *Reaction rate convection only.*
 Graph B. *Reaction rates with jet assisted convection.*

Rates of formation of carbon oxides during the pentane oxidation in Design B are given by Graphs B and C of Fig. 13. It will be noted that carbon monoxide formation reached a distinct maximum at 400° C., which has been found to be the temperature of the maximum rate of aldehyde formation. At temperatures of 450° C. and higher, rate of carbon monoxide formation was just measurable, reaction being substantially to the final products, carbon dioxide and steam. The small hump on the carbon monoxide graph at 650° C. might be attributed to error in measurement but it was obtained on several occasions and is believed to be genuine and possibly due to decomposition products that might be present in small proportion in spite of the high rate of oxidation.

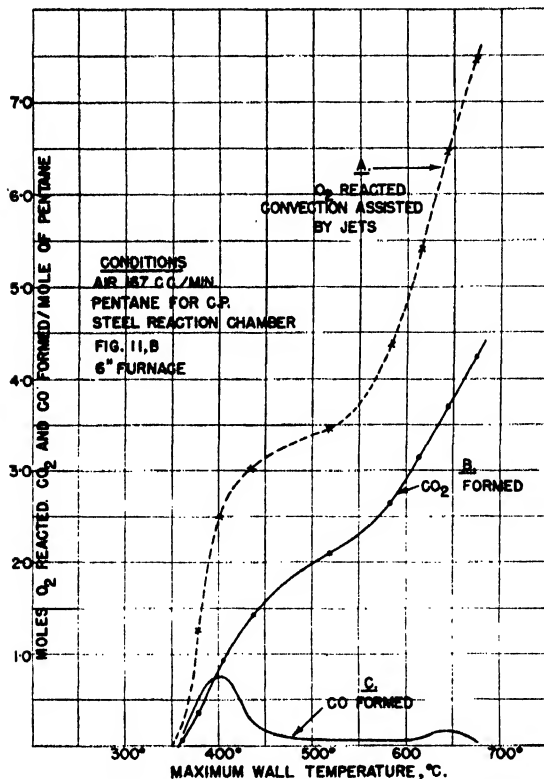


FIG. 13. Carbon dioxide and carbon monoxide formation in reaction with jet assisted convection circulation.

Section IV

REACTION VELOCITY AS AFFECTED BY THE FLOW CONFIGURATION IN REACTION CHAMBER No. 10

Pentane could be oxidized in Reaction Chamber No. 10 (2) at high velocity and the temperature raised, without the occurrence of explosion, until the reaction of oxygen was complete. The flow configuration within the chamber is, therefore, of interest and is indicated by the diagram, Fig. 14, drawn on an enlarged scale. The diameter of the chamber was 1.2 cm., the length 2.2 cm., and the material Jena Supramax glass. The reacting mixture entering through an orifice at the bottom of the chamber forms a streamline jet that impinges on the top surface of the chamber in suitable conditions of pressure and orifice diameter. The laminar flow in the jet is broken on the surface, the reacting mixture fans out on it and in order to reach the outlet at the bottom periphery of the chamber must move downward along the wall setting up a circulation as shown by the diagram. Eddies as vortex rings probably form between the ascending and descending streams but are not shown by the diagram because the exact flow configuration is speculative. It is important, however, to realize that the velocity of the ascending streamline

jet is greater than that of the stream of gas descending along the wall, in proportion to the respective path areas. The area of cross section of the path of the jet from a 1.0 mm. diameter orifice is 0.0078 cm.^2 and that of the return path down the wall, assuming a layer 2.0 mm. thick, is 0.63 cm.^2 . Therefore, if gas were supplied at the rate of 100 cc. per min. to the unheated chamber, the

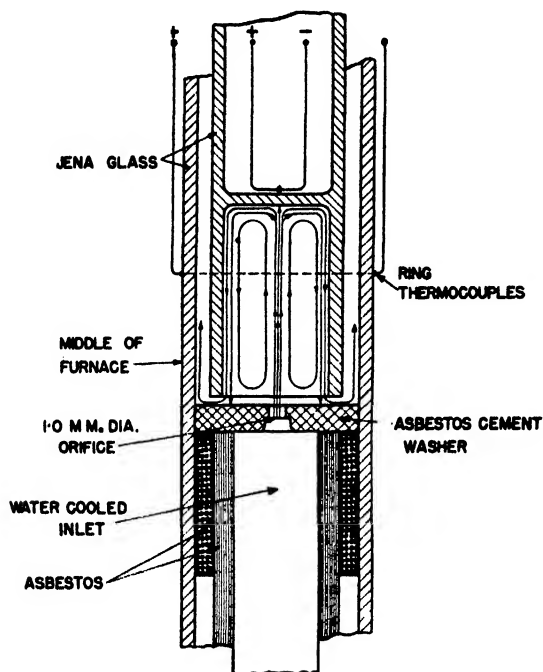


FIG. 14. Diagram of reaction chamber No. 10.

velocity of the jet would be 217 cm. per sec. and that of the descending stream 2.6 cm. per sec. and still less if the stream were thicker than 2.0 mm. The conclusion is that gas flowing through the chamber has a scouring effect on a small circular area of surface of which the position of impact of the jet is the center. The considerations advanced and the experiments described in Sections II and III indicate that reaction to partial products proceeds at an appreciable rate only over the small area mentioned, the remainder of the surface of the chamber being of little practical importance. Experiments supporting this view will now be described.

Effect on Reaction Rate of Changing the Velocity of the Jet While Maintaining a Constant Rate of Gas Supply

Pentane-air in combining proportions was supplied at 50 cc. per min., orifice diameters of 1.0 mm. and 0.5 mm. being used. The velocity of the jet from the larger orifice would then be 108 cm. per sec. and that from the smaller one 432 cm. per sec. if the coefficient of discharge were unity. It was verified by separate experiments, using smoke to make the air flow visible, that the jets

retained a streamline form over the distance from the orifices to the position of impact on the top of the reaction chamber. The velocity of the stream of gas descending along the wall would be unchanged and the sole difference in flow configuration would occur in the small circular area of which the position of impact of the jet is the center. Rates of reaction are shown by the graphs of Fig. 15, and it will be seen that on changing from the larger to the smaller

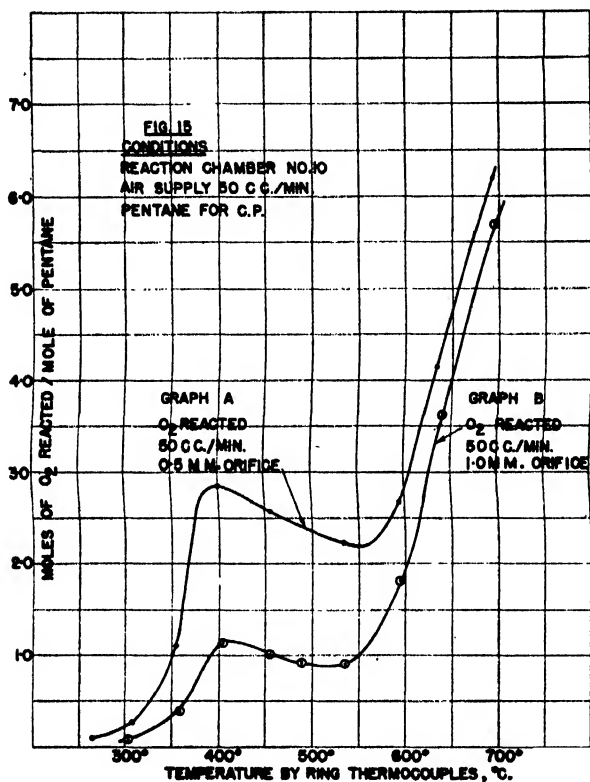


FIG. 15. Effect of jet velocity, reaction chamber No. 10, with constant rate of mixture supply.

orifice, reaction velocity increased over the whole temperature range of the experiment. The increase was greatest at the temperature of the formation of partial oxidation products at the maximum rate and was then nearly 150%. It is to be remembered that rate of aldehyde formation was limited because the reacting mixture contained one mole only of pentane to eight moles of oxygen and therefore all of the pentane could be oxidized to aldehyde by the reaction of one-eighth of the available oxygen.

Effect on Reaction Velocity of Increasing the Proportion of Pentane in the Mixture with Air

The graphs of Fig. 16 show reaction velocities for pentane-air supplied to reaction chamber No. 10 through a 1.0 mm. orifice. Graph A gives rates of oxygen reacted when the mixture contained two moles of pentane to eight

moles of oxygen and Graph B gives rates of oxygen reacted when the mixture contained one mole of pentane to eight of oxygen. The experiments were made in similar conditions of flow configuration and of all other respects and show, as would be expected from considerations already discussed, that the

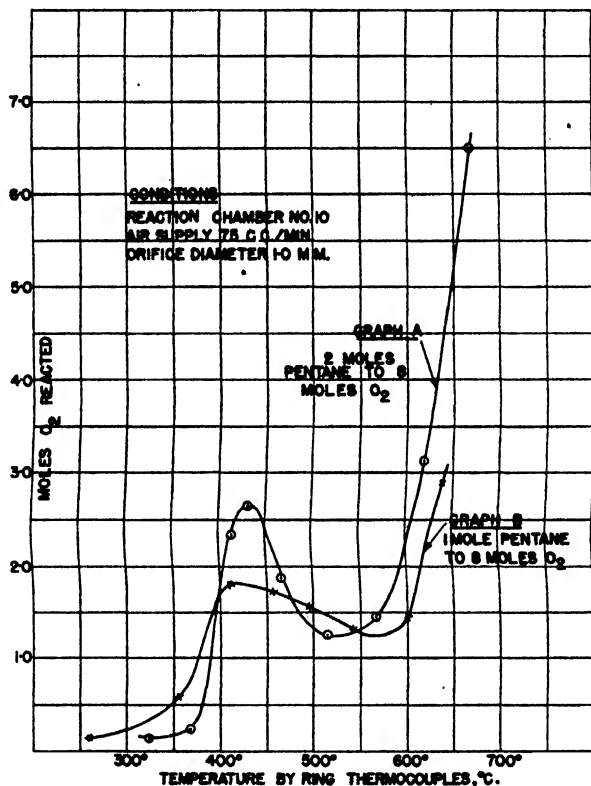


FIG. 16. *Effect of increasing pentane concentration in mixture with air, reaction chamber No. 10.*

removal of partial oxidation products from a relatively small area of active surface by the scouring action of the jet allows access of unreacted mixture and the formation of such products at a greatly increased rate if the composition of the reacting mixture permits. Thus, the aldehyde hump of Graph A is exceptionally pronounced and maximum rate of reaction at the corresponding temperature is 70% greater than for the mixture containing half as much pentane and oxidized in the same conditions of flow configuration.

Effect on Degree of Oxidation of Time of Exposure and Flow Configuration

When a reacting mixture is supplied to reaction chamber No. 10, having a volume of 2.5 cc., at the rate of 50 cc. per min., the time of exposure to the oxidizing conditions, as usually calculated, is 3.0 sec. and the flow configuration is fixed by the diameter of the admission orifice. The rate of supply being increased to 150 cc. per min., the time of exposure is reduced to 1.0 sec.

but if the diameter of the orifice remain unchanged, flow configuration is altered by the velocity of the jet having increased by 300% with a corresponding increase in the scouring effect on the surface on which the jet impinges. The results of experiments made accordingly are given by the graphs of Fig. 17 and it will be seen that over the low temperature range a maximum of

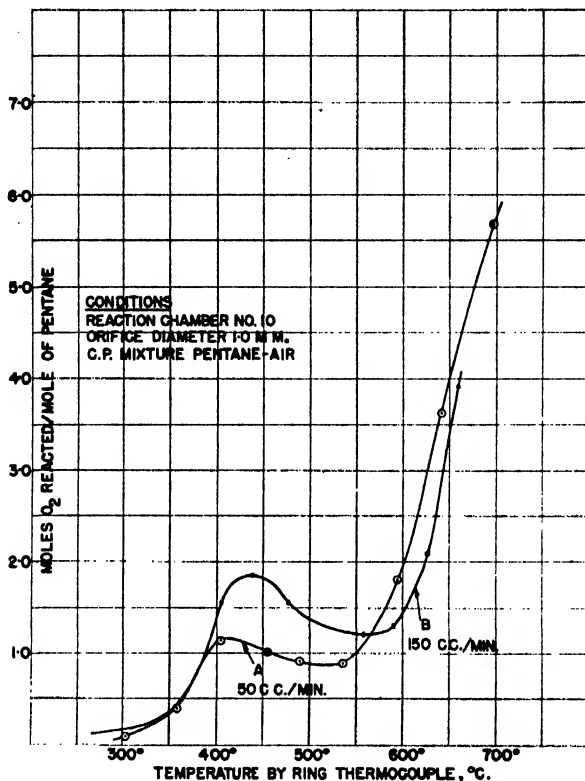


FIG. 17. Effect of threefold increase in rate of mixture supply, reaction chamber No. 10.

1.8 moles of oxygen was reacted in the 1.0 sec. exposure time and 1.2 moles only in the 3.0 sec. time. Even over the higher range of temperature for which reaction is mainly to final products the increase of 300% in exposure time accounted for a relatively small decrease in moles of oxygen reacted.

Section V

CONCLUSIONS

The experiments described in preceding sections were concerned with the oxidation of pentane in air but the results are probably of more general application. It is suggested for discussion and for further experimental work—

(a) That the reduction in reaction velocity obtained on packing an open combustion space is not due to an increase of surface but to the consequent change in the flow configuration of the reacting mixture.

(b) That the oxidation of pentane is a heterogeneous reaction, velocity depending on flow configuration and the nature of the surface of the reaction space. The graphs of Fig. 18 are given in support of the suggestion.

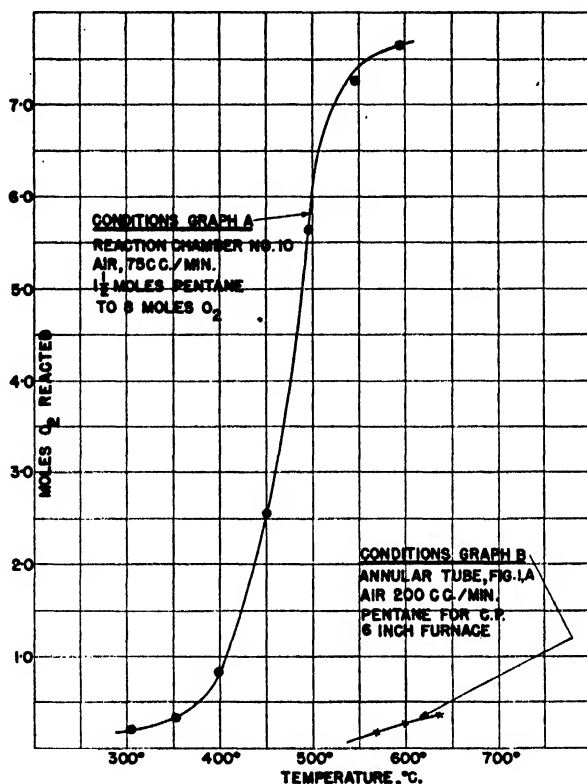


FIG. 18. Nearly complete or nearly zero reaction depending on flow configuration and nature of surfaces.

Graph A, showing a remarkable rate of oxidation with completion of the reaction without explosion at 600° C., was obtained for an oxidation in reaction chamber No. 10 of pentane containing iron carbonyl in the concentration of 0.67%. The mixture with air contained 50% more pentane than required for combining proportions. The reacting mixture was, as shown by the experiments of Part I, brought, by the flow configuration in the reaction chamber, into intimate contact with a small surface area of iron maintained in an oxidizing atmosphere by continuous deposition from the carbonyl. In spite of the extremely high reaction velocity, oxidation was, at all temperatures, straight through to carbon dioxide and steam, no more than a trace of aldehyde or carbon monoxide being found in the products.

Graph B was obtained in conditions of nearly laminar flow combined with an inactive surface for a mixture of pentane with air in combining proportions. The steel annular combustion tube A, Fig. 1, was used for the experiment and the surface was rendered inactive in respect of the carbon dioxide steam

reaction by a catalyst poison, ethyl mercaptan, added to the pentane in the concentration of 2%. It will be seen by reference to the graphs that reaction *began* at about the temperature of completion in the conditions used to obtain Graph A, and increased relatively slowly with further increase of temperature.

Acknowledgments

The experimental work described in this paper is part only of that carried out in the Colloid Science Laboratory, Cambridge, with the co-operation of Prof. E. K. Rideál and Dr. F. H. Garner.

The laborious and accurate gas analyses work was undertaken by Mr. R. R. Davidson, Emmanuel College, Cambridge, to whom credit is given for improvements in methods of using the Ambler apparatus.

Dr. E. W. R. Steacie and Dr. L. Marion, both of the National Research Council, have assisted by reading the text and advising accordingly.

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A Continuous Laboratory Vacuum Evaporator

In connection with several projects conducted in these laboratories, it was found necessary to concentrate large volumes of solutions *in vacuo*. A simple, rapid method for doing this was desirable, and a continuous evaporator, designed according to the principle of the rising film vertical tube evaporator (1, 2, 3), and suitable for the concentration of solutions tending to bump or foam, was built. This apparatus has been used extensively for the concentration of aqueous calcium glucopentahydroxypimelate solutions, and butyl acetate solutions of sulphite waste liquor resins.

Apparatus (Fig. 1).—This consists essentially of five parts, the boiler, the catchall, the condensate receiver system, the concentrate overflow (and level control), and the concentrate receiver system. Each part is joined to the

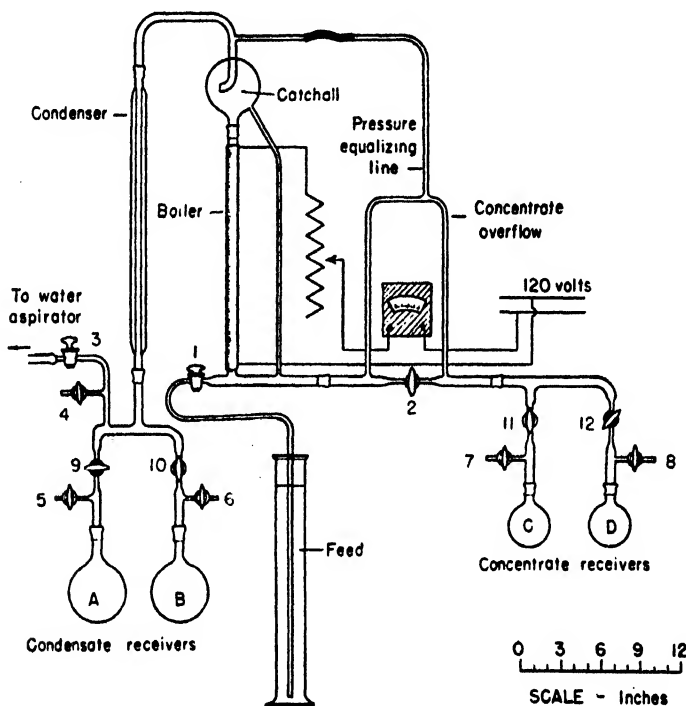


FIG. 1. Continuous vacuum evaporator.

next by 24/40 joints. The boiler is tightly wound for its entire height with nichrome wire, insulated with several layers of water-glass impregnated asbestos, and connected externally as indicated to give a power input of from 100 to 200 watts. The boiler is connected at the top, through a 500 ml. catchall, to the condenser, which in turn is connected to the condensate receiver system. The horizontal tube of the evaporator is connected through the concentrate overflow to the concentrate receiver system. By tilting the

latter forward, the level of the feed in the boiler may be varied, so that regardless of the nature of the solution, the evaporator tube is kept wet for its entire height, preventing evaporation to dryness and possible charring at any point in the tube. The entire apparatus is mounted on a board, with the bottom tube at an angle of 10° to 15° from the horizontal to facilitate draining.

Operation.—The apparatus is connected to an aspirator through Stopcock 3, and, with Stopcocks 3, 9, 10, 11, and 12 open and all others closed, the evaporator is evacuated to the desired extent. The vacuum may be controlled by use of a vacuum regulator, or by bleeding air in through Stopcock 4. Stopcock 1 is then opened and feed allowed to enter the apparatus to the desired level in the evaporator tube. Stopcocks 1, 9, and 11 are then closed, and the evaporator tube heated. Boiling begins within one minute, the liquid in the evaporator tube surging into the catchall. Stopcock 1 is opened slightly to permit continuous feed of the liquid, and the level overflow device tilted until a slow but steady amount of concentrate flows over and is collected in Receiver D. It is essential that feed surge into the catchall in order to keep the entire evaporator tube wet, as previously described.

The following data were obtained on the concentration of a butyl acetate resin solution:

Pressure in apparatus—18 mm. Hg,
 Temperature of feed entering— 20° C.,
 Average heat input—136 watts,
 Boiling temperature— 30° C.,
 Volume of butyl acetate evaporated—19.8 ml. per min.,
 Area of glass surface—0.25 sq. ft.,
 Average power input—136 watts = 1960 cal. per min.,
 Latent heat of vaporization of butyl acetate—65 cal. per ml.,

$$\text{Heating efficiency of evaporator} = \frac{65 \times 19.8}{1960} \times 100 = 66\%.$$

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AN INVESTIGATION OF THE MACBETH ILLUMINOMETER¹

By W. E. KNOWLES MIDDLETON² AND A. R. RAMSEY³

Abstract

The MacBeth illuminometer is a well known portable photometer of the visual type. Measurements of its errors show that the instrument gives reliable results if used with care. The most serious errors may occur when the color temperature of the light that is being measured differs greatly from that of the working standard lamp in the instrument. Under such conditions, different observers may obtain widely different results.

Introduction

The MacBeth illuminometer (3, p. 13; 7, p. 7) is a portable photometer of the visual type, well known to illuminating engineers and optical physicists. It is deemed unnecessary to describe the instrument in detail, because of its wide distribution, but attention should be drawn to the fact that a separate reference standard lamp permits frequent recalibration of the working standard in the instrument. Because of the conditions under which portable photometers are used, this provision adds greatly to the accuracy of the illuminometer.

Of late years, illuminating engineers have come to rely more and more on photoelectric photometers for portable use, and it is probable that these are amply accurate for their purposes if frequently checked. The MacBeth illuminometer, however, has found wide and increasing use in physical researches for many kinds of incidental photometry, and physicists have frequently used it in situations where an older generation would probably have had recourse to much more elaborate apparatus. In all of this they have displayed a confidence in the instrument possibly justified but not very well documented. These considerations led the authors to undertake a study of the MacBeth illuminometer.

A few statements are to be found in the literature regarding the accuracy of portable photometers in general. In their instructions for making illumination surveys (2) the I.E.S. (New York) assign a round figure of $\pm 5\%$ to such measurements. The British Standards Specification (1) for visual-type portable photometers demands an accuracy of $\pm 10\%$. A study by A. K. Taylor

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(6) is even more pessimistic, but in this he was concerned with a miscellaneous group of instruments, obviously not operated by experienced physicists. In another study (5) Taylor considered that a photometer of the general type that we are considering "should be capable of repeating readings to within 2 per cent" (5, p. 359). The departure of the test surface from the cosine law was studied in some detail by Taylor, who found this to be the most important source of systematic error.

Wetzel and Gouffé (8), on the basis of a careful analysis of all the sources of error, suggest a "mean probable error" (square root of the sum of the squares of the individual maximum errors) of 6% for an illuminometer of this type. In their analysis, the test plate contributes little to the total error.

Since the error due to test plates of various materials has been investigated thoroughly by Taylor (5), the present work was confined to three aspects of the problem:

- (1) The error due to the necessity of adjusting the current through the working standard.
- (2) Temperature errors in the milliammeter.
- (3) Photometric errors.

In addition, some measurements of illumination were made indoors under practical conditions in order to make an estimate of the reproducibility of such measurements.

Errors Due to Current Adjustment

In the use of the MacBeth illuminometer, the current through the working standard lamp has to be adjusted to a certain value previously determined by photometry of a test plate illuminated by the reference standard. The adjustment is made by means of a rheostat and the current read on a milliammeter. The rheostat and meter supplied with the instrument are of high quality, the meter being provided with an antiparallax mirror.

To test the possible precision of this adjustment, a potentiometer was connected across a 0.1 ohm standard resistor placed in series with the rheostat, milliammeter, and lamp. The current could be read on the potentiometer to better than 0.1 ma. with ease. Settings were made on one of the divisions of the meter scale, and also on an arbitrarily chosen current (e.g. 228.5 ma.) between the divisions, which are at intervals of 5 ma. Care was taken to avoid parallax by placing the eye so that its image in the meter-scale mirror coincided with that of the pointer.

It soon became apparent that the rheostat itself is the limiting factor. At normal lamp currents, the passage from one turn of the rheostat to an adjacent turn changes the current by about 0.4 ma. or 0.2%. When the meter was being set on a line, the potentiometer readings indicated that one or other of two adjacent rheostat turns was almost always chosen. When it was being set between divisions, one of three turns would usually be taken. In either case, the uncertainty produced is of the order of 0.2%.

In the ordinary use of the illuminometer, the current is set to the nearest milliamperere. In view of the properties of the rheostat, it is of doubtful value to attempt a closer setting than this, and we may therefore conclude that the maximum error that should be expected from this cause is 0.2% in current.

A variation of 0.2% in current represents a change of 1.5% in light output. This was determined for the working standard by photoelectric photometry, using a G.E. barrier-layer cell and 'zero-resistance' circuit (4). The cell with its correcting filter was tested for spectral response and found to approximate the visibility curve of the normal eye. Now there are three current settings involved in a complete series of measurements: (a) reference standard lamp current, (b) setting of working standard lamp current to make brightness match with reference standard, and (c) setting current through working standard during measurements. It is possible that the three errors might all be of the same sign, in which event their sum (expressed in light output) could reach 4.5%. The square root of the sum of the squares of the three errors is 2.6%, but note that the distribution of such errors is not at all normal.

Temperature Errors of Milliammeter

The milliammeter was calibrated at three temperatures by the Electrical Measurements Section of the National Research Council, through the kindness of Mr. A. J. Grant. It was found that a change of 10° C. in temperature produced an error of 0.2% in current, or 1.5% in light output. A decrease in temperature will cause the illuminometer to read high. Thus if the working lamp were compared with the reference standard indoors, and the instrument then taken outdoors for measurements, in winter, large errors might result.

Photometric Errors

The MacBeth illuminometer is comparatively seldom used to measure light at the same color temperature (about 2400° K.) as that from its working lamp. For this reason it is important to know the errors of heterochromatic measurements as well as homochromatic ones. It might be expected that measurements with a color match would be much more reproducible than those with a large color difference.

In this investigation, the color temperatures used were 2400°, 2840°, 3500°, and 6000° K., the two highest being obtained by the use of blue glass filters. The transmittance of these filters was carefully measured with a König-Martens spectrophotometer and the color of the light calculated in the usual way. The working lamp of the illuminometer was operated at a color temperature of 2440° K. throughout.

A magnesium oxide surface about 12 cm. square was set up normal to the axis of the photometer bench, and a well-aged lamp mounted on one of the movable carriages. The voltage on this lamp was controlled to $\pm 0.02\%$, so that less than 0.1% scatter would be produced in the observations by voltage fluctuations. The magnesium oxide surface was observed at an angle

of about 45°, the illuminometer being clamped in position to minimize the fatigue of the observers in the rather long series of observations involved. In order to make sure that the clamping of the instrument did not alter the precision of the readings, 48 sets of 10 readings each were made, half with the illuminometer held in the hand. Each entry in Table I shows the percentage probable error* of the mean of 10 readings under the stated conditions. It will be seen that there is no systematic difference.

TABLE I

PROBABLE RANDOM ERROR (%) OF THE MEAN OF 10 SETTINGS OF A MACBETH ILLUMINOMETER, USING TWO METHODS OF SUPPORT

Color temp.	Illumination (about)					
	3 l. ft. ⁻²		10 l. ft. ⁻²		20 l. ft. ⁻²	
	Clamped	Hand-held	Clamped	Hand-held	Clamped	Hand-held
2440	0.40	0.57	0.44	0.85		
	0.74	0.47	0.66	0.83		
	0.61	0.47	0.62	0.57		
	0.55	0.28	0.54	0.44		
2840			0.99	1.00	1.02	0.92
			0.63	1.13	1.24	0.99
			1.04	0.89	1.06	1.00
			0.71	0.69	1.17	1.09
3500			1.28	0.97	0.80	1.00
			0.84	1.42	1.72	1.09
			1.33	1.13	1.38	1.15
			1.36	1.37	0.58	1.14

With the apparatus set up as described, two series of readings were taken, each on six successive days, a complete set covering both observers and four color temperatures being taken each day. In order that the error of reading the milliammeter should not enter, the current through the working standard was measured with a potentiometer as described above. At the beginning of each day's observations, the working lamp of the illuminometer was standardized by comparison with the reference standard.

The results of this investigation are summarized in Table II. It should be emphasized that each entry in this table is the result of 60 readings taken over six days, so that any variation in the actual value of the illumination will also be included. It is believed, however, that this was less than $\pm 0.1\%$.

It will be noted that in the homochromatic case, the difference between the observers was of the same order of magnitude as the probable error, but at the higher color temperatures the difference became much more important. No explanation is suggested for the much greater difference between the

* The probable error of the mean of N readings is defined as $P = 0.6745 \sqrt{\frac{\sum v_i^2}{N(N-1)}}$.

TABLE II

PROBABLE ERROR (%) OF A SET OF 10 READINGS AT VARIOUS COLOR TEMPERATURES, DERIVED FROM SIX SERIES OF 10 READINGS EACH. WORKING STANDARD LAMP AT 2440° K.

Color temp. °K.	Observer A		Observer B		Difference 100 (A-B)/A, %
	Illumination l. ft. ⁻²	Probable error, %	Illumination l. ft. ⁻²	Probable error, %	
2440	2.86	±0.90	2.89	±1.34	-1.0
	10.08	0.42	10.10	0.93	-0.2
2840	11.41	0.49	11.28	0.32	+1.1
	18.3	0.64	18.3	1.88	0.0
3500	9.69	1.42	8.73	2.32	+9.9
	18.0	2.24	16.3	1.77	+9.4
6000	3.53	1.19	3.48	2.78	+1.4
	6.91	3.34	6.63	2.94	+4.0

observers at 3500° than at 6000° K., except that one or both of them must have adopted different criteria of equality at the two temperatures. There is no tendency towards greater precision at the higher of the two values of illumination.

The probable error of a single reading is about three times that of the set of 10 readings, assuming a normal error curve. Since a deviation 2.4 times as great as the probable error may occur once in 10 readings, it will be seen that at a color temperature of 3500° K., a single observation might be in error by about 15% once in 10 times. Even the average of a set of 10 readings might be in error by 5%. With a color match, this is reduced to 1% or at the most 2%.

Errors in Practical Use

The experiments described in the preceding section were made under laboratory conditions, corresponding to the type of use that is made of the instrument by many physicists. It was felt desirable to supplement these measurements by some observations of the kind that would be made by illuminating engineers in the course of a lighting survey, although it is realized that photoelectric photometers have largely replaced visual ones for such purposes.

A 500-watt frosted lamp was hung in a fixed position in a large room that could be darkened. This lamp was run from a storage battery and the voltage controlled to about 0.02%. Four stations were established in the room to permit the test plate to be placed in the same position on successive days. The walls of the room were cream-colored with a reflection factor of about 0.60, the color being approximately Munsell 5Y8/4, and most of the equipment in the room was black in color. The color of the illumination was therefore sensibly that of the light from the lamp, 2820° K.

Each day for six days the illuminometer was first checked against the reference standard, and then four readings were made by each of two observers at each of the four selected stations. The entries in the body of Table III are the means of these sets of four readings. The penultimate line in the table

TABLE III

DAILY MEASUREMENTS IN A ROOM ILLUMINATED BY A LAMP AT A COLOR TEMPERATURE OF 2820 K. AVERAGES OF FOUR READINGS ON EACH OCCASION. ILLUMINATION IN LUMENS PER SQUARE FOOT.

Day	Position							
	1		2		3		4	
	Observer							
	A	B	A	B	A	B	A	B
1	2.62	2.64	7.03	7.22	4.41	4.71	16.5	16.3
2	2.59	2.59	7.15	7.47	4.57	4.59	16.2	16.4
3	2.60	2.64	7.06	7.20	4.34	4.62	16.6	16.5
4	2.66	2.64	6.90	7.09	4.54	4.81	17.1	16.3
5	2.62	2.59	6.81	6.92	4.43	4.54	16.8	16.7
6	2.64	2.68	6.91	7.01	4.55	4.63	16.5	16.5
Mean	2.62	2.63	6.98	7.15	4.47	4.65	16.6	16.5
Probable error of four settings, %	0.66	0.89	1.20	1.82	1.41	1.40	1.25	0.66
Difference between observers, %, 100(A-B)/A	-0.4		-2.4		-4.0		+0.6	

gives the probable error of a set of four readings. It should be noted that this includes the error resulting from the daily standardization of the illuminometer lamp against the reference standard. The probable error is in all instances less than 2%, so that it becomes unlikely that the mean of four readings will be in error by more than 5%, as far as photometric errors are concerned.

Another series was run later as a check with the lamp at a color temperature of 2915° K., but the results are so similar that they will not be given.

Attention is directed to the considerable, and somewhat erratic, differences between the two observers. As the sets of observations were made at Positions 1 to 4 in immediate sequence, it is improbable that either observer would change his criterion of brightness match between the various positions. The good correspondence between the results for successive days makes such an explanation even more unlikely. It seems probable, therefore, that the greater part of the scatter in these differences is due to the obstruction of part of the illumination by the body of the observer. Each observer probably took, at each station, a stance that seemed comfortable, and repeated this fairly closely each day. It should be noted that this source of error also operates in the use of photoelectric illuminometers.

Conclusion

The conclusion that may be drawn from all these measurements is that the systematic errors are considerably more important than the random ones. Considered as a photometer apart from the external conditions of its use, the MacBeth illuminometer has excellent properties. Where only relative readings are required, and especially with light of a constant color, the mean of a few settings will almost certainly give a precision of $\pm 5\%$, and if an approximate color-match can be obtained, this can be improved to $\pm 2\%$. In laboratory use, the additional error due to the current setting can be reduced to negligible proportions by the use of a potentiometer and a standard resistance.

On the other hand, serious systematic errors can enter into the use of the instrument even under laboratory conditions, when light of high color temperature is being measured. It is desirable that the color vision of the observer should be known to be normal, or at least that his Y/B ratio (7, p. 263) should be nearly unity, before any reliance is placed on such measurements.

When it is necessary to measure illumination coming from several or all directions, an uncertainty is bound to arise from the obstruction of some of the light by the body of the observer. This can be minimized only with care in selecting a stance in relation to the incident light. The recommendations of Taylor (5) regarding the test plate should be followed. The test plate furnished with the illuminometer is of a material (pot opal glass) found by Taylor to be the most satisfactory of all materials studied. An angle of view of 30° to the normal was found to be the best. One may conclude that the figure for the precision, $\pm 5\%$, suggested by the I.E.S. (2) is of the right magnitude and certainly not too great.

Finally, the instrument should not be subjected to a large change of temperature between calibration and use.

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CANADIAN WILTSHIRE BACON

XXX. EFFECTS OF CURING AND COOKING ON THE THIAMINE, RIBOFLAVIN, AND NIACIN CONTENTS OF LONGISSIMUS DORSI MUSCLES¹

BY DYSON ROSE² AND RUTH PETERSON²

Abstract

Laboratory studies on the thiamine, riboflavin, and niacin contents of longissimus dorsi muscles and of spent pickle indicate that there was little or no destruction of these vitamins during the curing process but that approximately 24% of the thiamine, 12% of the riboflavin, and 29% of the niacin were leached from the meat. The losses due to leaching increase with greater relative pickle volumes and are greater from an exposed surface of lean meat than from a surface covered with fat or rind. The commercial practice of rebuilding spent pickle probably reduces the over-all vitamin losses.

The losses of thiamine and of riboflavin incurred during the cooking of pork were found to be considerably greater than those incurred during the cooking of bacon. Niacin was lost to about an equal extent from both pork and bacon. The stabilization of the thiamine and riboflavin that occurred during the curing process was sufficient to offset the losses during cure and thus, after cooking, bacon was as good a source of these vitamins as pork.

Introduction

The B-vitamin content of pork has been estimated in several laboratories but the losses incurred during the conversion to bacon have not been studied extensively. Jackson and his coworkers (4) determined the retention of thiamine, riboflavin, and niacin following "wet cure" of bacon and found a loss of thiamine, niacin, and probably riboflavin, but the loss varied considerably from sample to sample. McIntire *et al.* (5) report values for the thiamine and niacin contents of "Canadian bacon" that are somewhat below the usual values for fresh pork, indicating that a loss may have occurred during processing. Schweigert and coworkers (11) have also reported losses of thiamine, riboflavin, and niacin from pork hams during cure. Working in these laboratories, Gorham (2) found lower thiamine, and niacin contents of Wiltshire half-backs after curing in pickle but found no significant change in the riboflavin content.

The results of numerous studies on the effect of cooking on the vitamin content of pork and pork products have indicated that 10 to 50% of the thiamine, 10 to 25% of the riboflavin and 0 to 20% of the niacin may be lost (1, 2, 9). Variations in the losses have been related to differences in the type of product studied and in the time, temperature, and method of cooking (4, 7, 8, 11). The studies of Rice *et al.* (8), of Nymon (6), and of Gorham (2) have indicated that the stability of these vitamins may be influenced by the

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admixture of other materials into the pork products and by the curing processes. The work of Gorham (2) appeared particularly interesting as it indicated that a change occurring during the curing of Wiltshire bacon stabilized the niacin against subsequent loss during cooking.

The studies reported in the present paper were undertaken to determine the fate of the vitamin lost from the meat, the effect of variations in the Wiltshire curing process on the extent of the loss, and the effect of commercial curing on the vitamin losses during subsequent cooking.

Analytical Methods

The methods used for estimating the vitamin content of the lean meat were essentially the same as those previously described (2), thiamine by the thiochrome procedure, riboflavin by a fluorometric method, and niacin by microbiological assay. At first, pickle samples were assayed without preliminary hydrolysis but it was found that hydrolysis increased the thiamine assay values, and an enzymic hydrolysis of a 1 : 10 dilution of the spent pickle was made for all subsequent thiamine assays. For convenience, niacin assays were also made on the hydrolyzed samples although the hydrolysis had no significant effect on the results. The 10-fold dilution, which was necessary to avoid salt inhibition of the hydrolytic enzymes, was too great to permit subsequent riboflavin assay. Hydrolysis with sulphuric acid was tried but the assays were of low accuracy owing to the high salt (sodium chloride plus sodium sulphate) concentration. All pickle samples were therefore assayed for riboflavin directly by a microbiological procedure, with sufficient dilution to avoid serious interference from the sodium chloride. The technique used was essentially that of Snell and Strong (12), but the basal medium was modified by doubling the yeast extract, tripling the dextrose, and adding 6 gm. of crystalline sodium acetate and 20 ml. of casein hydrolyzate (General Biochemicals Ltd.) per 500 ml. of basal medium.

Moisture and chloride determinations were made on the lean meat samples by methods previously described (3). The results of analysis of variance of the dry weight data did not differ essentially from those of the moist weight data, so the assay values, with the exception of those for the cooking experiment, are reported as $\mu\text{gm. per gm.}$ of fresh or cured lean meat. For comparison the vitamin content of the pickle is also reported as $\mu\text{gm. per gm.}$ of meat, the conversion from $\mu\text{gm. per ml.}$ of pickle being made by multiplying by the pickle : meat ratio.

Experimental

Variability in Materials

Rice *et al.* (9) and others have shown that a considerable variation in vitamin content may occur from muscle to muscle in a single hog as well as in the same muscle from different hogs. In the present work the variability was reduced as much as possible by making all determinations on the longissimus dorsi muscles. Marked variations were found even within this muscle (Table I) although the variation between samples from one hog was less than

TABLE I

VARIATIONS IN VITAMIN CONTENTS (μ GM. PER GM.) OF LONGISSIMUS DORSI MUSCLES
IN FRESH PORK

Vitamin	Between 11 different hogs		Between 10 samples from the same hog	
	Range	Average	Range	Average
Thiamine	8.1 - 15.4	12.3 \pm 2.1	13.2 - 13.8	13.5 \pm 0.2
Riboflavin	1.30 - 1.76	1.50 \pm 0.15	1.54 - 1.84	1.65 \pm 0.11
Niacin	26.7 - 78.7	53.5 \pm 4.5	35.3 - 42.2	40.9 \pm 2.1

that between hogs. The data indicated a slight decrease in the vitamin content from the fore end to the back of the hog but the differences were significant (5% point) for riboflavin only.

Effect of Salt Concentration and Duration of Cure

To determine the effects of brine concentration and pickling time random sections of longissimus dorsi muscles weighing approximately 200 gm. each were immersed individually in brines containing 1% sodium nitrate, 0.05% sodium nitrite, and 15, 22.5, or 30% sodium chloride. Curing times of zero to seven days at 40° F. and a meat : pickle ratio of 4 : 3 (by volume) were used. All samples were ground shortly after removal from the pickles and were stored at -10° F. until analyzed. The spent pickle was stored at 30° F. until analyzed (about six weeks); prolonged storage did not significantly affect the assay values. The experiment was conducted in triplicate. Thiamine, riboflavin, and niacin were determined on the meat and spent pickle, and chloride and moisture determinations were made on the meat.

The chloride content of the meat increased with curing time and with pickle concentration, the final (seven day) values averaging 5.72, 7.25, and 9.02% for the meat from the 15, 22.5, and 30% brines respectively. Moisture content of the meat decreased with time and with brine concentration, being 73.1% in the fresh meat and 71.1, 69.4, and 67.5% after seven days cure in the 15, 22.5, and 30% brines.

Table II shows the average thiamine, riboflavin, and niacin contents of the meat and spent pickle together with the necessary differences for significance. The salt concentration did not significantly affect the distribution of thiamine or niacin but the amount of riboflavin found in the pickle increased with increasing salt concentration (average values 0.10, 0.13, 0.14 μ gm. per gm. for the 15, 22.5, and 30% pickles respectively; necessary difference for significance, 5% level, 0.015).

These data show that although only the thiamine and niacin content of the meat decreased significantly during cure, all three vitamins accumulated in the pickle. Riboflavin, as well as thiamine and niacin, must therefore have been lost from the meat but the losses involved were small relative to the

TABLE II

DISTRIBUTION OF THIAMINE, RIBOFLAVIN, AND NIACIN ($\mu\text{GM. PER GM OF MEAT}$) IN PORK AND PICKLE DURING CURE

Days in pickle	Pickle	Meat	Total
Thiamine			
0	—	13.2	13.2
1	1.2	11.3	12.4
2	1.6	9.9	11.4
3	2.2	9.8	12.0
4	2.5	9.7	12.1
5	2.7	9.1	11.9
6	3.2	9.2	12.4
7	3.2	9.2	12.4
Necessary difference ^a	0.46	1.49	—
Riboflavin			
0	—	1.46	1.46
1	0.06	1.36	1.42
2	0.09	1.39	1.48
3	0.12	1.36	1.47
4	0.14	1.46	1.60
5	0.13	1.23	1.36
6	0.16	1.31	1.47
7	0.17	1.40	1.57
Necessary difference ^a	0.023	—	—
Niacin			
0	—	57.3	57.3
1	7.9	41.6	49.5
2	9.4	36.0	45.4
3	11.4	36.1	47.5
4	12.5	38.0	50.5
5	15.7	41.9	57.7
6	16.6	38.0	54.6
7	15.7	34.3	50.0
Necessary difference ^a	3.6	11.0	—

^a Necessary difference for significance, 5% point.

variability between samples and are thus masked when the assay values for the meat are considered. The average amount of vitamin in the pickle at the end of the seven day cure represented 24.2% of the thiamine, 11.8% of the riboflavin, and 29.0% of the niacin originally present in the meat. Since the total amount of each vitamin remained constant within the limits of experimental error, these figures also represent the approximate percentage loss from the meat under these conditions.

Effect of Rind and Fatty Tissue.

Three samples of spent pickle obtained from a commercial packer were assayed and were found to contain 1.1 $\mu\text{gm.}$ of thiamine, 0.06 $\mu\text{gm.}$ of riboflavin, and 3.1 $\mu\text{gm.}$ of niacin per gram of meat cured. These results are lower than those obtained in the laboratory work and it appeared probable that the greater area of lean and cut surface exposed to the pickle during the laboratory cure had allowed a greater amount of vitamin to leach from the

meat. To test this assumption all but one of the lean surfaces of 10-in. central sections from the right sides of three hogs were covered with lard and the sections were immersed in 30% brine. At the end of a seven day curing period at 40° F. the sections were sliced longitudinally and the slices of longissimus dorsi, trimmed free of fat, were apportioned so as to give four samples of approximately 125 gm. each taken at increasing depths below the exposed surface. The left sides from the same hogs were similarly sliced when fresh to serve as controls.

The losses, expressed as average differences between the corresponding control and cured samples, are given in Table III. The loss of thiamine and niacin decreased markedly as the distance from the exposed surface increased, but the losses of riboflavin were too small to show significant variations.

TABLE III

AVERAGE LOSSES OF THIAMINE, RIBOFLAVIN, AND NIACIN FROM CURED PORK SAMPLED AT VARIOUS DEPTHS BELOW A SINGLE EXPOSED SURFACE

(Averages for three hogs, μ gm. per gm. of meat)

Approx. depth, in.	Thiamine	Riboflavin	Niacin
0 - 0.4	5.6	0.07	34.0
0.4 - 0.8	2.2	-0.10	21.7
0.8 - 1.2	0.7	-0.10	10.1
1.2 - 1.6	1.0	0.03	7.5
Necessary difference, 5% point	1.31	—	9.88

Effect of Meat : Pickle Ratio

Six random sections of the longissimus dorsi muscles from each of three hogs were used to determine the effect of increasing the volume of brine relative to the meat. A brine of 1.0% sodium nitrate, 0.05% sodium nitrite, and 30% sodium chloride was used at meat : pickle ratios of 1.0 : 0.5, 1.0 : 0.8, 1.0 : 1.0, 1.0 : 1.3, and 1.0 : 2.0 by volume. The samples were cured individually for seven days and were then ground and stored at 40° F. until analyzed.

The thiamine, riboflavin, and niacin contents are given in Table IV. Significant quantities of thiamine and niacin, but not of riboflavin, were lost from the meat to the pickle. A slight over-all loss of thiamine occurred during this experiment. The losses of thiamine and of niacin increased considerably as the volume of pickle relative to the meat increased and the loss of riboflavin increased slightly but not significantly.

Effect of Rebuilding Pickles

In commercial practice, spent Wiltshire pickles are usually rebuilt and reused and an attempt was therefore made to assess the effect of this practice on the vitamin losses. The vitamin contents of a series of commercial pickles

TABLE IV

DISTRIBUTION OF THIAMINE, RIBOFLAVIN, AND NIACIN IN PORK AND PICKLE AFTER CURE AT VARIOUS MEAT : PICKLE RATIOS

(Averages for three hogs, $\mu\text{gm.}$ per gm. of meat)

Meat : pickle ratio	Pickle	Meat	Total
Thiamine			
Fresh meat	—	11.2	11.2
1.0 : 0.5	2.7	8.1	10.8
1.0 : 0.8	2.8	7.3	10.1
1.0 : 1.0	3.2	7.4	10.6
1.0 : 1.3	3.9	5.9	9.8
1.0 : 2.0	4.1	6.0	10.1
Necessary difference ^a	1.03	1.36	0.78
Riboflavin			
Fresh meat	—	1.51	1.51
1.0 : 0.5	0.13	1.44	1.57
1.0 : 0.8	0.16	1.47	1.63
1.0 : 1.0	0.17	1.47	1.64
1.0 : 1.3	0.20	1.35	1.55
1.0 : 2.0	0.23	1.37	1.60
Necessary difference ^a	—	—	—
Niacin			
Fresh meat	—	55.0	55.0
1.0 : 0.5	10.6	35.0	45.6
1.0 : 0.8	14.8	35.2	50.1
1.0 : 1.0	17.6	36.3	53.9
1.0 : 1.3	19.5	34.3	53.8
1.0 : 2.0	19.0	30.1	49.1
Necessary difference ^a	3.25	9.22	—

^a Necessary difference for significance, 5% point.

increased only slightly during reuse (for three consecutive batches, thiamine 1.1, 1.1, 1.2; riboflavin 0.05, 0.05, 0.07; niacin 2.8, 3.0, and 3.4 $\mu\text{gm.}$ per gm. of meat). Some of the processes used to clarify and rebuild pickles were applied on a laboratory scale and the results are presented in Table V. These results do not necessarily correspond to those that would be obtained under commercial conditions but they indicate that much of the vitamin should be retained in the rebuilt pickle unless carbon black is used as a decolorizing agent.

Effect of Storage and Cooking

Six fresh (pork) and six cured (bacon) rib-in export backs were obtained from a commercial packing concern. These were cut into two pieces and the pieces were individually wrapped in wax paper, overwrapped with kraft, and stored at 30° F. Duplicate cured and uncured pieces were removed at weekly intervals and cut into slices 3 to 4 mm. in thickness. Alternate slices of the longissimus dorsi muscles, trimmed free of extraneous tissue and fat, were used to constitute the cooked and uncooked samples.

TABLE V

VITAMIN CONTENT OF PICKLE AFTER CLARIFICATION, $\mu\text{GM. PER ML.}$

Treatment of 500 ml. aliquots of pickle	Thiamine	Riboflavin	Niacin
Control	1.1	0.07	5.4
Slurried with 1.6 gm. 'Filter Cel' and filtered	1.1	0.04	5.2
Slurried with 1.0 gm. 'Norit' and filtered	0.4	0.02	1.3
Heated in boiling water bath 60 min., filtered	1.2*	Nil	5.7*

* No correction applied for evaporation.

The slices for the cooked sample were broiled until thoroughly done but not browned (500° F. for three minutes on one side, one minute on the other). Both samples were ground and stored at -40° F. until analyzed.

The moisture content of all samples tended to decrease during storage but the losses did not reach the level of statistical significance. During cooking the average moisture content dropped from 70.9 to 56.0% for the pork and from 71.7 to 61.7% for the bacon.

The riboflavin and niacin contents of the samples did not vary significantly during storage but the thiamine content increased irregularly during the first three weeks of storage and then fell again. Although this rise was statistically significant for both the fresh and dry weight data it was probably the result of random differences in the thiamine content of the backs as purchased.

The average vitamin contents of the meat samples before and after cooking are given, on a dry weight basis, in Table VI, together with the percentages

TABLE VI

THIAMINE, RIBOFLAVIN, AND NIACIN CONTENT OF UNCOOKED AND COOKED PORK AND BACON AND THE PERCENTAGE OF EACH VITAMIN RETAINED IN THE COOKED MEAT

(Averages for all storage times, dry weight basis)

	Bacon	Pork	Difference
Thiamine			
Uncooked, $\mu\text{gm. per gm.}$	56.7	51.3	+ 5.4
Cooked, $\mu\text{gm. per gm.}$	55.0	42.6	+12.4**
Retention, %	97.3	83.2	+14.1**
Riboflavin			
Uncooked, $\mu\text{gm. per gm.}$	5.85	6.60	- 0.75*
Cooked, $\mu\text{gm. per gm.}$	5.64	4.86	+ 0.78*
Retention, %	97.6	73.7	+23.9**
Niacin			
Uncooked, $\mu\text{gm. per gm.}$	193.1	269.7	-76.6*
Cooked, $\mu\text{gm. per gm.}$	174.9	228.7	-53.8*
Retention, %	91.3	88.3	+ 3.2

* Significant to the 5% level.

** Significant to the 1% level.

retained in the cooked samples. The retention of each of the three vitamins in the cooked samples was not significantly affected by storage, but, except for niacin, was greater in the bacon than in the pork.

Discussion and Conclusions

The data obtained during these experiments indicate that little or no destruction of the vitamins occurs during the curing of bacon. With the exception of thiamine in one experiment, all of the vitamin of the fresh meat was present in the meat and pickle at the end of the experiment. Vitamin losses from the meat are, therefore, due to leaching into the pickle. The extent of this leaching is influenced by the amount of exposed lean surface and the volume of pickle, but not, except with riboflavin, by the pickle concentration. The significant effect of pickle concentration on the riboflavin content of the spent pickle can not readily be explained.

Throughout the curing experiments no attempt was made to duplicate commercial practices and the figures for vitamin losses are not to be taken as representative of those incurred in packing plants. Gorham (2) has reported losses of 21.5% for thiamine, 2.7% for riboflavin, and 30.8% for niacin when half-backs were cured on a semicommercial scale using fresh pickle, and Jackson (4) reported average losses of 25.9% of the thiamine, 11.0% of the riboflavin, and 19.2% of the niacin during "wet cure" of bacon on a similar semicommercial basis. These figures do not differ markedly from those obtained in the present work using small pieces of lean meat (24.2% of the thiamine, 11.8% of the riboflavin, and 29% of the niacin). The additional data presented on the effect of the relative amount of pickle, and of the area of lean meat exposed to the pickle, indicate that these results are all high, and that commercial use of a maximum meat : pickle ratio, the curing of whole sides, and the use of rebuilt pickles probably reduce the losses materially.

The results of the cooking experiment are not in complete agreement with those of Gorham (2). The data show that the losses of thiamine and of riboflavin caused by cooking are significantly lower from bacon than from pork, thus confirming a trend suggested by the data of Gorham. But, on the other hand, no significant differences in the percentage of niacin retained in the cooked samples were found in the present work. The samples were cooked for a shorter time (four minutes) than that used by Gorham (six minutes) and the moisture content of the cooked samples was considerably higher (Table VII). With the exception of riboflavin in pork, the losses incurred during cooking were therefore not as great. The losses from bacon were particularly small and any effects of storage were not significant.

The data in Table VII show that the moisture content of the cooked samples was more variable than that of the uncooked samples but the variation is not excessive and the degree of cooking appears to have been satisfactorily controlled. It is interesting to note that there is a significant difference between the moisture content of pork and bacon after cooking for four

TABLE VII

MOISTURE CONTENT OF PORK AND BACON BEFORE AND AFTER COOKING

	Source of data			
	Gorham ^a (averages of duplicates)		Present work (single determinations)	
	No. of samples	Moisture, %	No. of samples	Moisture, %
Uncooked pork	4	73.5 ± 0.79	12	70.9 ± 2.45
Cooked pork	4	50.5 ± 1.50	12	56.0 ± 3.37
Uncooked bacon	10 ^b	69.9 ± 1.71	12	71.7 ± 1.62
Cooked bacon	10 ^b	48.7 ± 3.98	12	61.7 ± 3.02

^a Private communication.^b Data for 10 samples cured to contain a salt and nitrite content similar to that obtained commercially.

minutes but not after cooking for six minutes. This difference between the data for the two cooking times makes it appear unlikely that the improved vitamin retentions in the cured samples that were cooked for four minutes are dependent upon the higher moisture retention. It seems probable that the Wiltshire curing process effects a certain degree of stabilization of thiamine, riboflavin, and niacin but the extent of the losses of these vitamins during cooking is influenced by the conditions used and pork and bacon do not necessarily respond equally to a change in the cooking procedure.

Rice *et al.* (7) have shown that the losses during the home cooking of cured ham were lower than those during the cooking of fresh hams. They related this difference to the less severe cooking conditions required with the cured meat. Our samples were cooked under rigidly controlled conditions and the differences found are entirely the result of changes effected in the meat by the curing process. It is conceivable that the differences observed by Rice and his coworkers may also have been due, in part, to a similar effect of the curing process.

The pork and bacon samples used by us were from different pigs and the data for the uncooked samples can not be used for estimating the losses of the vitamins during the curing process. They serve, however, to indicate the relative value of the pork and bacon as a source of these vitamins, and it is apparent from the data that the stabilization of thiamine and riboflavin effected by the curing process was sufficient to offset the losses incurred during processing of the bacon. The cooked bacon is thus a better source of these two vitamins than is the cooked pork. Niacin, however, was lost, during cooking under these conditions, to almost the same extent from both the pork and the bacon and the cooked bacon therefore appears to be a poorer source of this vitamin than the cooked pork.

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THE EFFECT OF BUILDERS IN HARD WATER DETERGENT SOLUTIONS¹

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Abstract

The water-softening ability of soda ash, trisodium phosphate, sodium metasilicate, tetrasodium pyrophosphate, and sodium hexametaphosphate was investigated. Each builder possessed great water-softening power and in each case the reaction with hardness was immediate and the residual hardness from maximum softening was less than 1 grain per gallon of water. The effect in detergent solutions of builders at concentrations that had given maximum softening in the above tests was investigated by determining soil removal, degradation, and deposit of insoluble compounds after 10 launderings of standardly soiled flannelette. In these relatively high concentrations the alkaline builders gave inferior detergency to that of soap alone in hard water. The sequestering agent, sodium hexametaphosphate, gave results that were superior to soap alone in hard water and equal to that of soap alone in soft water. In every instance the addition of builder before soap produced the same effect as builder with soap.

Although considerable data have been reported on the use of builders in soft water detergent solutions, experimental work involving the use of hard water has been limited. Cobbs, Harris, and Eck (6, 8) have made a comprehensive study of various combinations of builders with soap using concentrations up to 0.37% (builder and soap) in water of 300 p.p.m. hardness. Carter and Stericker (4) confined their work to the use of silicates in water containing temporary hardness. Bolton (3) used a variety of builders and made a study of the soap requirement for sudsing. The present work was undertaken in the hope of contributing more information on the action of builders in hard water solutions. Preliminary investigation involved a study of the water softening powers of a wide variety of builders with consideration of the rate and the extent of water softening. Further work involved a study of the detergent efficiency of the builders plus soap using the concentrations of builders that had given maximum water softening action. Study was also made to determine whether it would be best to add the builder to the solution before the addition of soap, or whether the combined addition of builder and soap as in a 'built soap' would be equally satisfactory. Estimation of detergent efficiency was made from Launder-Ometer washings of standardly soiled fabric. The extent of soil removal was determined by reflectance readings and chemical degradation by cuprammonium fluidities. A rough estimate of the build-up of insoluble compounds was obtained from determination of the percentage ash after 10 washings.

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Experimental

The compounds used were sodium carbonate, trisodium phosphate, sodium metasilicate, tetrasodium pyrophosphate, and a sodium phosphate glass with a molar ratio of Na_2O to P_2O_5 somewhat greater than that corresponding to the empirical formula of NaPO_3 . For convenience this latter compound will be termed 'sodium hexametaphosphate'. A synthetic hard water (3) that would be best representative of natural waters was used. Thus all experimental work was carried out in water containing hardness equivalent to 17.5 grains per U.S. gallon of calcium carbonate (300 p.p.m.) and a calcium:magnesium ratio of 2 : 1 in terms of calcium carbonate. A stock solution containing 35 grains per gallon calcium carbonate equivalent (600 p.p.m.) was prepared by dissolving 0.6035 gm. of 73.5% calcium chloride (c.p. grade) and 0.4060 gm. magnesium chloride ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, c.p. grade) in 1 liter of distilled water. The soap* used was believed to be representative of a neutral soap made from an average amount of saturated and unsaturated fatty acids. For hardness determinations a standard soap solution was prepared according to the procedure of the American Public Health Association (1) so that 1 ml. of the solution was equivalent to 1 mgm. of calcium carbonate.

The procedure for hardness determinations was such that all determinations were made as closely as possible to 60° C. The sample bottles (250 ml.) were supported in a wooden rack suspended in a water bath adjusted to 60° C. A burette was mounted above the rack to enable titrations to be made while the bottles were in the bath and thereby prevent much loss of heat during titrations. Preparatory to each determination of hardness, a 25.0 ml. volume of the stock solution of hard water (600 p.p.m.) was pipetted into a 250 ml. glass stoppered bottle. Freshly boiled and cooled distilled water was run in from a 25.0 ml. burette so that with the addition of the desired quantity of a stock solution of builder the total volume would be 50.0 ml. The bottle was placed in the rack for a 40-min. warming period before the builder solution was added from a 5.0 ml. graduated pipette. The bottle was shaken. After the desired interval of time, i.e., either immediately or after 30 min., standard soap solution was titrated into the bottle a small amount at a time. The bottle was shaken vigorously after each addition and soap solution was added until a lather lasted for five minutes when the bottle was placed on its side. To minimize any change of temperature, the bottle was placed horizontally on top of the rack during the time necessary for the observation of lather. The volume of the sample was increased by the addition of soap solution but since this change was due to 80% grain alcohol it was considered negligible. The volume of standard soap solution required to give a permanent lather when multiplied by 20 gives the total hardness as the equivalent of calcium carbonate as parts per million.

Ten wash tests were made in a Launder-Ometer (2) on samples (3 in. \times 4½ in.) of standardly soiled flannelette.† Flannelette, a napped fabric, was

* Colgate Palmolive Peet Golden XXX Powdered Soap.

† Prepared at the National Research Council of Canada, Ottawa. The soiling medium was a mixture of lampblack, Nujol, and lanoline applied from a trichlorethylene bath.

chosen in order to offer a large surface for adsorption of insoluble matter that might be deposited from the detergent solutions. For each builder eight samples were prepared, four being subjected to treatment whereby the builder was added to the water before soap and four whereby the builder and soap were combined before being added to the water. For each set, half the samples were saved for measurement of soil removal and degradation and half for measurement of insoluble compounds. The latter samples were weighed before washing to enable the estimation of percentage ash based on the original fabric.

All washings were done in the presence of 0.50% soap at 60° C. in Launder-Ometer bottles containing 100 ml. (measured at 20° C.) solution. To standardize the procedure, as well as for convenience, stock solutions of water, builder, and soap were prepared. The method of mixing the solutions of builder and soap was (A) adding builder before soap and (B) adding builder at the same time as soap. In each case, the desired volume of water was measured by a graduated cylinder into a Launder-Ometer jar containing 10 rubber balls. The bottle was placed in the Launder-Ometer until the water reached 60° C. For Method A, 10.0 ml. of builder solution was pipetted into the bottle and the solution was mixed by slight agitation, then 10 ml. soap solution (at 60° C.) was added by pipette. For Method B, 10.0 ml. pipettes containing builder and soap were held so that the solutions from both pipettes ran into the bottle in a single stream. In either case the solution was mixed; the sample was added; the bottle was returned to the Launder-Ometer. At the end of the 15 min. washing period, the sample was put through a wringer, subjected to two three-minute rinses at 60° C. in water softened by builder, and one three-minute rinse at 60° C. in untreated water (300 p.p.m.), wrung, and allowed to dry.

It might be mentioned that the purpose of adding builder to the first two rinse waters was to prevent precipitation of soap in the washed fabric by hard water salts.

Controls of soap alone were as follows: 0.50% soap in distilled water; 0.50% soap in hard water; 0.73% soap in hard water (since in measurements of water softening ability it was found that 0.23% soap was required to precipitate the hardness).

Extent of soil removal was determined by use of the Hunter Multipurpose Reflectometer (9). Two readings were made from each sample and the results from duplicate samples were averaged. Chemical degradation was estimated from cuprammonium fluidities (8). An estimation of the amount of insoluble matter deposited from the detergent solutions was made by ashing the washed samples and by calculating the ash as percentage weight of the original untreated samples. Ashing was done in a muffle furnace at dull red heat to prevent fusion of phosphates and thereby permit combustion to be complete.

Data

Water Softening Ability

The volume of standard soap solution required to produce permanent suds is shown in Table I basing the concentrations of builders on the as-weighed basis as grams per milliliter of solution and in Fig. 1 basing the concentrations on the anhydrous basis. Titrations when soap was added immediately after the builder and when soap was added 30 min. after the builder were similar

TABLE I

STANDARD SOAP SOLUTION REQUIRED FOR PERMANENT SUDS IN 100 ML. HARD WATER
(300 P.P.M. CALCIUM CARBONATE EQUIVALENT) CONTAINING BUILDER

Concentration of builder, gm./100 ml.	Standard soap solution for sudsing in presence of builder, ml.				
	Soda ash	Trisodium phosphate	Sodium metasilicate	Tetrasodium pyrophosphate	Sodium hexameta- phosphate
0.05	14.78				10.00
0.09	11.12				
0.10	11.09	3.86			6.45
0.15	11.32				
0.20	11.75	3.66		4.66	0.45
0.25					0.35
0.30	14.00	2.92			0.23
0.40		2.35		2.32	0.23
0.45	11.10				
0.50		1.59	12.80	0.98	
0.60	9.55	1.13		0.52	0.23
0.65		0.89			
0.67		0.80			
0.70				0.31	
0.73		0.73			
0.75	8.89	0.73	9.00		
0.80		0.73		0.16	0.23
0.85				0.10	
0.90	7.81			0.05	
1.00		0.73	6.25	0.05	
1.50	5.55		2.46		
1.75			1.04		
2.00	3.93		0.66		
2.25			0.56		
2.50	1.64		0.47		
2.60	1.60				
2.70	0.80				
2.75	0.60		0.47		
3.00	0.60		0.47		
3.50	0.60				
4.50			0.47		

in every instance, consequently only the single values are listed. It is to be noted that for each builder there was a decrease in the amount of soap required for sudsing with increase of builder concentration until a concentration was reached beyond which the amount of soap required for sudsing did not change. The completeness of the water softening varied with the builders. Data pertaining to the lowest concentrations of the builders required to give maximal softening are given in Table II. It is to be noted that the residual hardness

ranged from 1 p.p.m. using tetrasodium pyrophosphate to 15 p.p.m. using trisodium phosphate. The concentration of builder required for maximum softening increased in the following order: sodium hexametaphosphate, trisodium phosphate, tetrasodium pyrophosphate, sodium metasilicate, and soda ash. On the anhydrous basis the trisodium phosphate concentration is

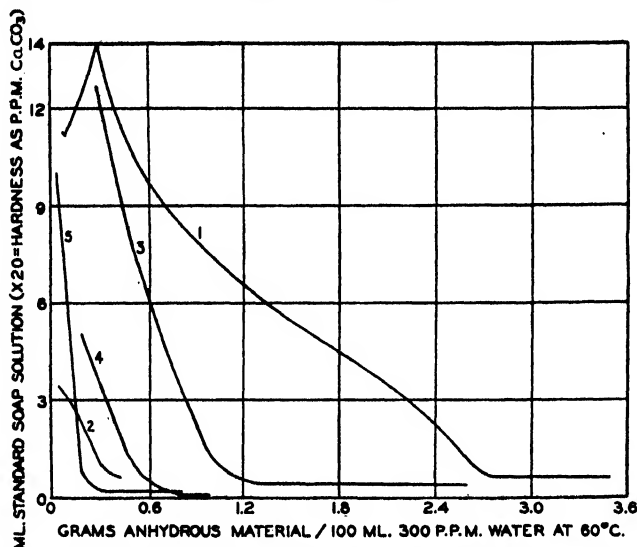


FIG. 1. Standard soap solution required for permanent suds in 100 ml. water at 60° C. (300 p.p.m. calcium carbonate equivalent hardness) containing builder.

1. Soda ash. 2. Trisodium phosphate. 3. Sodium metasilicate. 4. Tetrasodium pyrophosphate. 5. Sodium hexametaphosphate.

TABLE II

LOWEST CONCENTRATION OF BUILDERS ADDED TO HARD WATER (300 P.P.M. CALCIUM CARBONATE EQUIVALENT) FOR MAXIMUM SOFTENING

Builder	Residual hardness, p.p.m.	Concentration of builder, gm./100 ml.		No. of equivalent weights of builder: 1 equivalent weight of hardness*
		As weighed	Anhydrous	
Soda ash	12	2.75	2.75	86
Trisodium phosphate	15	0.73	0.32	10
Sodium metasilicate	9	2.50	1.44	40
Tetrasodium pyrophosphate	1	0.90	0.90	22
Sodium hexametaphosphate	5	0.30	0.30	5**

* Obtained by dividing the number of equivalent weights of builder per liter solution by the number of equivalent weights of hardness per liter solution (0.006).

** In the absence of data regarding the exact composition of Calgon the formula was assumed to conform to that of sodium hexametaphosphate.

practically equal to the sodium hexametaphosphate concentration and the concentration of sodium metasilicate appears appreciably lower than that of soda ash. It is interesting to note the wide variation in the ratio of the number of equivalent weights of builder to one equivalent weight hardness. These ratios are in agreement with the arrangement of builders according to builder concentrations.

A factor of considerable importance is the manner of softening the water. Soda ash, trisodium phosphate, and sodium metasilicate caused the removal of hardness by precipitation. Tetrasodium pyrophosphate removed hardness by formation of precipitates and soluble complexes depending on the relative amounts of phosphate and hardness. Sodium hexametaphosphate formed soluble complexes with the hardness.

Soil Removal

The extent of soil removal based on the increase of brightness over the reflection readings of the original soiled cloth are given in Table III. An

TABLE III

DETERGENT EFFICIENCY DATA BASED ON INCREASE OF BRIGHTNESS AFTER 10 WASHES

Substance	Units of brightness increased		Efficiency (0.50% soap in distilled water = 100)		Efficiency index (efficiency: concentration)	
	Builder added before soap	Builder added with soap	Builder added before soap	Builder added with soap	Builder added before soap	Builder added with soap
<i>I. Builder solutions</i>						
Soda ash	10.7 ± 1.5*	11.3 ± 0.6	46	48	0.5	0.5
Trisodium phosphate	16.5 ± 0.3	16.9 ± 1.1	70	71	7	7
Sodium metasilicate	13.1 ± 0.3	13.2 ± 0.5	56	58	1	1
Tetrasodium pyrophosphate	15.9 ± 0.4	16.7 ± 0.5	68	71	3	3
Sodium hexametaphosphate	21.6 ± 0.2	21.6 ± 0.5	92	92	18	18

II. Controls

0.50% soap in distilled water	23.5 ± 1.3	100	
0.50% soap in hard water (300 p.p.m.)	18.2 ± 0.5	78	
0.73% soap in hard water (300 p.p.m.)	18.7 ± 0.8	80	

* Standard error.

analysis of variance made on the results shows that the difference between Methods A and B is not significant; the difference between treatments is significant. Making allowance for standard error it is apparent from Table III that the difference between the distilled water control and the sodium hexametaphosphate treatment is not significant whereas the difference between

the distilled water control and any of the other treatments is significant. The treatments tend to take the following order of decreasing efficiency: 0.50% soap in distilled water, sodium hexametaphosphate, 0.50% soap in hard water, 0.73% soap in hard water, trisodium phosphate, tetrasodium pyrophosphate, sodium metasilicate, and soda ash. By placing the increase in brightness of the distilled water control at 100 and calculating the other values accordingly, the efficiencies of the solutions may be rated. An economical builder from the standpoint of deterative efficiency is one that gives a high efficiency when used in low concentration. A comparison of the builders based on both efficiency and concentration is given by the efficiency index obtained by dividing the efficiency by the number of equivalent weights of builder that reacted with one equivalent weight of hardness in water softening (from Table II). The efficiency indices show differences among builders having similar values for increase in brightness; trisodium phosphate has an efficiency index higher than that of tetrasodium pyrophosphate; sodium metasilicate has an efficiency index higher than that of soda ash. The superior position of sodium hexametaphosphate above the other builders is emphasized by the efficiency index.

Degradation

There was no significant difference between the fluidity of the original untreated material and that of any of the washed samples. Therefore chemical degradation and tensile strength loss from each washing procedure for 10 washings must be considered nil.

Deposit of Insoluble Compounds

When allowance is made for experimental variation, it becomes apparent from Table IV that the manner of addition of builder and soap did not affect the percentage ash. On the basis of percentage ash, the treated samples may be divided roughly into three groups: 0.50% soap in distilled water, and sodium hexametaphosphate; 0.73% soap in hard water, 0.50% soap in hard water, and tetrasodium pyrophosphate; trisodium phosphate, sodium metasilicate, and soda ash. Factors that might influence the ash of the samples are the fabric, the soil, and deposits from the detergent solutions. Since the washing procedure causes removal of soil and consequently a decrease in amount of ash attributed to the soil, any increase in ash must be caused by the detergent solution. The actual percentages of ash found by experimentation are in agreement with the manner of water softening by the substances concerned. For example, sodium hexametaphosphate, which formed a low percentage ash, formed soluble complexes with the hardness of water, whereas trisodium phosphate, sodium metasilicate, and sodium carbonate, which formed high percentage ashes, formed precipitates with hardness. Comparison with the controls of soap in hard water shows that the deposits formed from solutions of trisodium phosphate, sodium metasilicate, and sodium carbonate (i.e., calcium and magnesium hydroxides, phosphates, silicates, and carbonates) were considerably greater than the deposits from soap alone (i.e.,

lime and magnesium soap). This difference is typical of the behavior of inorganic and organic compounds. The higher ash from these builder solutions might also be caused by precipitates formed by builders with hardness in the first two rinses. The ash caused by tetrasodium pyrophosphate was

TABLE IV
ASH OF SAMPLES AFTER 10 WASHINGS

Substance	Ash, % of original weight	
	Builder added before soap	Builder added with soap
<i>I. Builder solutions</i>		
Soda ash	1.94	2.13
Trisodium phosphate	1.46	1.93
Sodium metasilicate	1.98	1.94
Tetrasodium pyrophosphate	0.89	0.64
Sodium hexametaphosphate	0.35	0.49
<i>II. Controls.</i>		
0.50% soap in distilled water		0.11
0.50% soap in hard water (300 p.p.m.)		0.65
0.73% soap in hard water (300 p.p.m.)		0.57
Original material		0.20

slightly higher than that by sodium hexametaphosphate yet considerably lower than that by the other builders. The explanation for this may lie in the action of tetrasodium pyrophosphate in the washing solutions. Solutions of tetrasodium pyrophosphate and hard water remained clear, probably owing to softening of water by dispersion or by sequestration of hardness. Addition of 0.50% soap to such solutions caused a cloudiness due to formation of a precipitate. Therefore it is possible that a precipitate was deposited on the fabric during washing and was not removed in rinsing operations.

The data show that the builders possessed great water softening ability and that the action in each instance was so rapid that the effect of the addition of builder before the soap was the same as that of the combined addition of builder and soap. With the exception of sodium hexametaphosphate, the builders gave results that were inferior to that from use of soap alone in Launder-Ometer tests.

Discussion of Data

In the determinations of water hardness no attempt was made to adjust the pH of the solutions. With the exception of sodium hexametaphosphate, which is nearly neutral, the substances would give pH values definitely on the alkaline side. It is possible that in alkaline solution, sodium hexametaphosphate might have lowered the final water hardness. The fact that less sodium

hexametaphosphate than tetrasodium pyrophosphate is required to remove hardness has been reported by Gilmore (7).

In the washing tests, with the exception of sodium hexametaphosphate, the builders in concentrations that were capable of giving maximum water softening did not improve the efficiency of soap alone in hard water. It is possible that these same agents did not possess great softening power under the conditions that existed in the washing tests, i.e., in the presence of 0.50% soap, in fact the agents might have given up the precipitated hardness to the soaps thereby precipitating them and reducing the washing efficiency of soap. Evidence that the maximum softening dosage of tetrasodium pyrophosphate did not hold in the presence of much soap is that this agent kept the water clear in the absence of soap but in the presence of considerable soap a precipitate formed. The same action might occur in the other alkaline baths but it would be masked by the alkaline precipitates. If this action were carried to completion the conditions for precipitation of hardness would be comparable to those existing in the solution of soap alone in hard water, i.e., the hardness would be precipitated solely by soap, consequently any deposit of insoluble material would be attributable to lime and magnesium soaps. However, in the presence of alkaline builders the percentage ash was greater than that produced with soap alone. Thus in the solutions containing alkaline builders the precipitation of hardness must be due at least in part to reaction with builder.

It is interesting to note that the actions of 0.50% soap and 0.73% soap in hard water were similar. Since 0.23% soap was probably used to precipitate the hardness it appears that, for detergent action after removal of hardness, 0.27% soap was as efficient as 0.50% soap. This is in agreement with work in soft water, which has indicated that soap concentrations beyond 0.25% are no more effective than that concentration (10).

In connection with measurement of chemical degradation it should be pointed out that the number of washings was of necessity limited to 10 and consequently no definite conclusions on the effects of these substances over long periods of washing can be drawn.

In relating the results of this work to large-scale operations, it seems probable that the same tendencies would be observed although the quantitative effects might not be the same; for instance, the build-up of compounds might not be as great since mechanical action would be more severe. It should be borne in mind that the concentrations of builders were those that gave maximum water softening and might not be the optimum concentrations for detergent efficiency. In fact, in the concentrations that were used the precipitation by builders reduced the detergent efficiency even more than the precipitation of lime and magnesium soaps alone. Harmful precipitates can be avoided by the use of a sodium phosphate glass, commonly termed sodium hexametaphosphate. The practice of using a 'built soap' would seem to be comparable to the technique of adding builder to the solution prior to the addition of soap.

Acknowledgments

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AN APPARATUS FOR DETERMINING THE SENSITIVITY OF GAS DETECTOR PAPERS¹

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Abstract

There is described an apparatus for determining the sensitivity of detector papers toward gases from liquids of low volatility. The paper holder is constructed in such a way that the papers may be moistened, dried, removed, or replaced without disturbing the flow of gas through the rest of the apparatus. The holder also makes possible the comparative testing, under identical conditions, of a number of papers. With auxiliary apparatus, the paper holder permits the use of a carrier air stream of controllable relative humidity.

Introduction

This apparatus was constructed and used to determine the sensitivity, to toxic agents of low volatility, of detector papers prepared by the impregnation of filter paper. Minor alterations in the auxiliary apparatus should permit its use with highly volatile agents. In operation, a stream of dry nitrogen or other inert gas is bubbled through the liquid toxic agent in such a way as to saturate the gas at the desired temperature. The saturated gas is diluted in a mixing chamber with air of controlled humidity. This diluted stream then passes in succession through a number of separate sheets of the detector paper under test.

Apparatus

The apparatus is illustrated in Fig. 1. The paper holder proper, *B*, is constructed of 22 mm. tubing (O.D.), its jacket of 40 mm. tubing bearing a 45/50 ground glass joint. The upper part of the jacket is ring-sealed to the main tube below the stopcock *A*. The lower part of the jacket is drawn off about 15 cm. below the joint and sealed to one arm of a U-tube, the other arm of which connects to the line by means of a 14/35 ground glass joint, *C*. (This U-tube is the only part of the apparatus that is constructed of 10 mm. tubing; the rest of the connecting tubing is 8 mm.) The 22 mm. tubing of the holder projects downward from the ring seal, passing about 2 cm. beyond the male member of the 45/50 joint. The end of this tube is ground square, polished, and fitted with hooks as illustrated. A 12 cm. length of 25 mm. tubing, selected to fit very snugly over the 22 mm. tubing has inserted into it a number of 15 mm. spacers of the 22 mm. tubing, the lowest of which is cemented into place.* (This is shown as a solid, heavy line in the drawing).

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* General Electric Glyptal Cement was found satisfactory for this purpose.

These spacers are cut square on the ends and polished to assure smooth fitting. The polishing was carried out on a wet felt disk charged with chromic oxide.

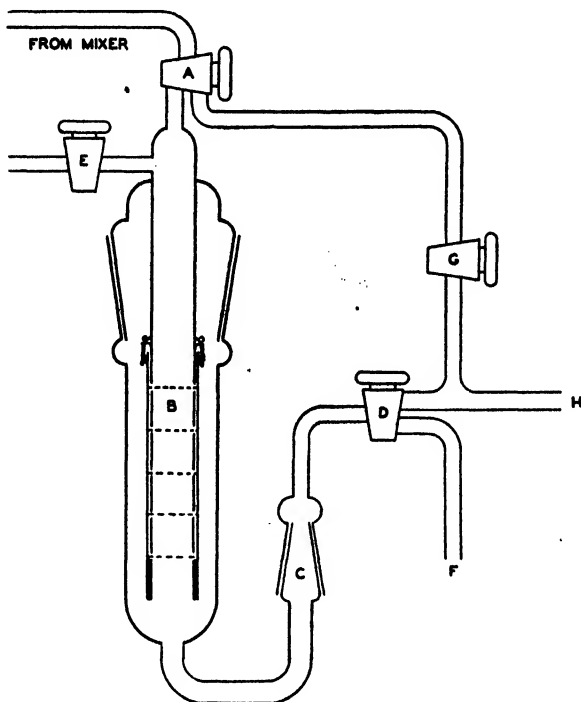


FIG. 1

In assembling the holder, a disk of detector paper (represented by a dotted line in the drawing) is inserted between each pair of spacers. The 25 mm. tubing, thus packed, is then slipped over the projecting end of the 22 mm. tube, the joint greased, and the springs fixed in place. The lower part of the jacket with its connecting U-tube and 14/35 joint is then clamped in place.

Operation

A stream of air of controlled humidity and controlled concentration of toxic agent enters the paper holder through the three-way stopcock, A. The moisture content of this air stream is adjusted by passing the air through a humidifier in parallel with a drier. The humidifier is composed of a glass jacket filled with 8-mesh Haydite* kept saturated with water. The drier is a second tube filled with 14-mesh silica gel.** By varying the relative rate of air flow through these two tubes, it is possible to obtain relative humidities (measured by means of a wet and dry bulb hygrometer) ranging from 30% to 95%. This air, of known humidity, is then passed through a

* An expanded shale aggregate, processed by the Cookville Company, Cookville, Ont.

** Davidson 'Protex-Sorb'.

flow meter and is led into a 1000 ml. bulb that acts as a mixer. Should completely dry air be required, the humidifier, drier, and hygrometer are by-passed by a phosphorus pentoxide drying tube constructed of a number of small tubes arranged in a larger tube and held in place by wax, the completed unit resembling a tubular boiler. The insides of the smaller tubes are covered with the drying agent and the inlet to the device is baffled to ensure passage of air through all the smaller tubes.

Into the mixer there also passes a stream of nitrogen saturated with the vapor of the reagent being used. This nitrogen (the commercial product) is dried thoroughly by being passed successively through calcium chloride and phosphorus pentoxide. The gas then passes through a flow meter and into a thermostated saturator similar to one described elsewhere (1).

The effluent from the mixer, which now contains a known concentration of water vapor and toxic agent, is passed into the paper holder as shown in the drawing. The air is drawn through the apparatus at a controllable rate by suction.*

As may be seen from the drawing, it is possible to load the paper holder with papers to be tested and then, by suitable manipulation of the stopcocks before admitting dry nitrogen to the saturator:

- (a) to dry or moisten the papers as desired either before or after a run by passing dry or water saturated air through the path *E-B-C-D-F*,
- (b) to bring the relative humidity of the diluent stream to the desired value through the by-pass *A-G-H*, without disturbing the papers in *B*,
- (c) to adjust the flow rate to the desired value, and to balance the resistance in the by-pass by means of the stopcock *G* to that of the papers in *B*.

This allows a duplicate run to be made, after reloading the paper holder *B*, without disturbing the flow rates.

When these adjustments have been made, the flow of gas may be regulated through the by-pass *A-G-H*, without being brought into contact with the papers. The flow is then directed through the paper holder by the path *A-B-C-D-H*, and the timing of the run begun. At the conclusion of the run, the metered flow is again diverted through the by-pass while the paper holder and the exposed papers are swept out with air through the path *E-B-C-D-F*.

It may be noted that a paper holder of this construction may be used to obtain information on the gas pickup per paper by passing the gas through several papers in series and noting the time of stain appearance on successive papers. Further, the use of papers in series has proved desirable for purposes of comparison.

Experimental

The results of an investigation of the sensitivity of two different detector papers to a toxic agent of low volatility are shown in Table I. Exposure of these papers to the vapor of the agent caused them to change color, and the

* An Electrolux cylinder (Model ZB 30) with a rheostat to control its motor speed was found to be suitable for this purpose.

purpose of the experiment was to determine whether or not the relative humidity of the air stream carrying the agent had any effect upon the sensitivity of the paper. For the data of Table I the following conditions obtain:

Flow rate of saturated stream (nitrogen) . . . 2.01 ± 0.05 ml. per min.

of diluent stream (air) 1070 ± 70 ml. per min.

Relative humidity of the nitrogen stream (dried
over phosphorus pentoxide) zero

The papers were 'conditioned' before exposure by passing water saturated air through them for 15 min.

TABLE I

R. H.* of air stream, %	Time of color appearance	
	Min.	Average, min.
Paper No. 1		
0	18, 15, >26, >30	>15
33 ± 1	9, 6, 5	6.5
50 ± 1	4.6, 4.8	4.7
64 ± 1	7, 6	6.5
95 ± 1	>26, >26	>26
Paper No. 2		
0	>26, >26	>26
33 ± 2	10, 11, 10, 10	10.5
50 ± 1	3.7, 3.9	3.8
63 ± 1	5, 3.4, 3, 3.8	3.8
95 ± 1	5, 4.7, 5	4.9

* R.H. = relative humidity.

If the saturator is assumed or known to be 100% efficient and the vapor pressure of the toxic agent at the temperature of the saturator is known, it is possible to calculate from the data the sensitivity of the detector paper expressed in terms of the weight of agent required to change the color of unit area of paper.

Discussion

It will be observed that the sensitivity of a detector paper to a toxic agent may be a function of the relative humidity of the air stream in which the agent is dispersed. Paper No. 1 has a considerably lower sensitivity at high and low humidities than it has at intermediate humidities. The maximum sensitivity of the paper would appear to be obtained when the relative humidity is about 50%. Paper No. 2, however, is almost as sensitive at 95% relative humidity as it is at 50%. Like Paper No. 1, its sensitivity at low relative humidity is very poor.

These phenomena make the evaluation of detector papers at different humidities very necessary if the true efficiency of the paper is to be determined.

Acknowledgments

The authors wish to thank Mr. D. A. Henderson and Mr. W. J. Allen for their assistance in the construction of parts of the apparatus. Mr. Allen also carried out the testing of the papers referred to in the text.

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INFLUENCE OF ORGANIC MATTER ON THE GERMICIDAL EFFICIENCY OF QUATERNARY AMMONIUM AND HYPOCHLORITE COMPOUNDS¹

C. K. JOHNS²

Abstract

Using *Staphylococcus aureus* and *Escherichia coli* as test organisms, the influence of various concentrations of skim milk on the germicidal potency of Roccal and of Dalglish hypochlorite solutions was studied. Both germicides retained their activity in the presence of unexpectedly high concentrations of skim milk, especially against *S. aureus*. Small concentrations frequently showed a slight potentiating effect in both laboratory and plant tests. The effectiveness of the hypochlorite fell off sharply beyond a certain concentration, while that of Roccal declined more gradually. Solutions of Roccal prepared with tap water were decidedly less active against *E. coli* than those prepared with distilled water. With the hypochlorite, tap water solutions were equally effective. Against *S. aureus*, a similar difference was noted although to a lesser extent. Added skim milk depressed the germicidal action of tap water solutions of Roccal to a greater extent than for distilled water solutions, while for the hypochlorite the reverse held true.

Introduction

In the sanitizing of equipment and utensils used in the handling and processing of food, considerable emphasis is usually laid upon the necessity of first removing all organic residue from the surfaces to be treated. While certain disinfectants, such as phenol, are effective in the presence of high concentrations of organic matter, the activity of others, such as the hypochlorites, is sharply reduced. Little published work has appeared, however, concerning the effect of low concentrations of organic matter, such as might be encountered by a solution used to sanitize food equipment. Prucha (13) showed the decline in available chlorine content when skim milk was added to several types of hypochlorite solution. Mallmann and Edwards (11) reported that a 20 p.p.m. solution of chlorine water, to which 0.2% skim milk had been added, was almost devoid of germicidal activity against *E. coli* after holding for 19 hr., even though it showed 10.4 p.p.m. chlorine by titration. They therefore warned against the re-employment of used chlorine solutions in the dairy industry, and in consequence their use was forbidden under the Standard Milk Ordinance of the U.S. Public Health Service (14).

In our studies with chlorine sterilizing agents in 1933 and 1934 (7, 8), a glass slide technique was developed in which the test organisms were present in a film of diluted skim milk on the surface of a sterile glass slide. When partially dried, the slide was gently agitated in the germicidal solution for the desired period, then plated. Despite the presence of the film of skim milk, almost complete destruction of the test organism was effected by the

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more active hypochlorite solutions within a few seconds. Similar results have been obtained in more recent studies comparing hypochlorites with quaternary ammonium compounds (9). Under the conditions of these tests, therefore, the presence of the film of skim milk did not depress germicidal activity significantly. This has raised some doubt as to the extent to which small amounts of organic matter, such as would be encountered on carelessly cleaned equipment, might interfere with the germicidal activity of both hypochlorite and quaternary ammonium solutions. The present studies were undertaken to throw more light on this point.

Methods

An alkyl dimethylbenzylammonium chloride (Roccal) was selected as a representative quaternary ammonium compound, while Dalglish Liquid Bleach (containing 10 to 12% available chlorine) represented the hypochlorites. During the first part of these studies, working solutions were prepared by diluting the original products with sterile distilled water. When it was subsequently found* that tap water solutions of quaternary ammonium compounds gave results quite different from those obtained from distilled water solution, Ottawa tap water was substituted as being more representative of the diluent used in plant practice. All concentrations were expressed as parts per million of active ingredient or available chlorine respectively.

Based on our previous findings (9), *S. aureus* (F.D.A. No. 209) and *E. coli* No. 117 were selected as representative test organisms. All testing was carried out with solutions at 20° C. Except where indicated, the glass slide technique previously described (9) was used, with the following slight modifications: (a) the slide, after agitation in the test solution for the required period, was rinsed in tap water for five seconds to minimize the carry-over of bacteriostatic concentrations of Roccal, and (b) the count on control slides was obtained by shaking the slide in 99 ml. of sterile saline, plating the slide itself and aliquots of the rinse, and calculating the total number originally present. (Studies over a considerable period showed that the five second rinse of the control slide in tap water removed an average of 81% of the number of cells of *S. aureus* originally present.) Bacto tryptone glucose agar (1) containing 7.5% sodium chloride to inhibit contaminants (3, 10), was used with *S. aureus*, and Bacto nutrient agar with *E. coli*. Plates were counted after incubation at 32° C. for 48 hr.

Skim milk was selected as the organic matter to be added, largely because of its homogeneity, uniformity from day to day, and of its representativeness of the type of residue likely to be encountered in the dairy industry. Comparative tests with homogenized and ordinary whole milks have given essentially the same results. Different results can be expected where other types of organic matter are used; preliminary tests with beef peptone broth, peptonized

* The author is indebted to Mr. C. T. Butterfield, U.S. Public Health Service, Cincinnati, Ohio, for the information that different water supplies gave different results with quaternary ammonium compounds.

milk, and sodium caseinate solution have shown all three to exert a greater depressing influence on the germicidal efficiency of Roccal than does skim milk, while peptone and gelatin are more nearly comparable to skim milk.

During the earlier studies, concentrations of Roccal and Dalglish were selected that would give approximately equivalent killing in the control solutions containing no added skim milk. In this way, it was felt that differences in reaction to added skim milk could be more readily observed. However, it subsequently became evident that the results of tests using 25 p.p.m. might differ significantly from those obtained at 100 or 200 p.p.m. Consequently, a further series of comparisons was made with both germicidal solutions at the same initial strength. These solutions were prepared from tap water instead of distilled water as in the previous tests, in order to simulate plant practice.

Experimental

Preliminary tests comparing Roccal 200 p.p.m. against Dalglish 50 p.p.m. led to the surprising discovery that the germicidal activity of the Roccal solution against *E. coli* was actually stimulated slightly by the addition of small amounts of skim milk. This aspect was therefore studied more exhaustively.

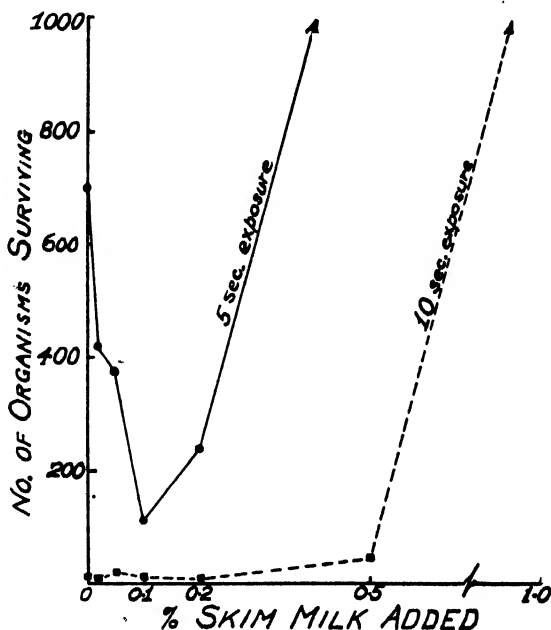


FIG. 1. Survival of *E. coli* as influenced by addition of skim milk to Roccal solution (200 p.p.m.). (Each point represents average of triplicate determinations.)

The results from a typical experiment appear in Fig. 1, wherein each point represents the average count from triplicate slides treated consecutively.

To check these findings, additional tests were conducted using a plating technique. In this, 1 ml. of standardized bacterial suspension was introduced

into 100 ml. of germicidal solution, kept agitated by a mechanical stirrer. At short intervals, 1 ml. portions were withdrawn, delivered into Petri dishes and immediately poured with agar medium. Several series of such tests were carried out, but as shown by the data from one of these (Table I) only a very slight potentiating effect could be detected. At concentrations up to 0.05%,

TABLE I

EFFECT OF ADDED SKIM MILK ON GERMICIDAL EFFICIENCY OF ROCCAL (50 P.P.M.) AS JUDGED BY THE PLATING TECHNIQUE. INOCULUM, *E. coli*, 7,500,000 CELLS PER ML. OF GERMICIDAL SOLUTION

% added skim milk	Count of survivors after exposure period, sec.					
	10	20	40	60	90	120
0	18	0	0	0	0	0
0.02	3	0	0	0	0	0
0.05	258	95	8	0	0	0
0.1	++++	+++	1000	76	6	0
0.2	++++	++++	++++	++++	++++	++++
0.5	++++	++++	++++	++++	++++	++++

N.B. Plus signs indicate relative density of colonies.

Bold-face type indicates point at which 99.9% destruction was noted.

the retarding influence was slight. At 0.1% (the concentration which showed maximum stimulatory effect by the glass slide method) a marked reduction in potency was indicated by the plating method. The lower concentration of Roccal employed in the latter (50 p.p.m. vs. 200 p.p.m. in the glass slide method) doubtless explains this difference; tests with 25 p.p.m. Roccal showed a definite retardation with only 0.02% added skim milk.

Attention was next directed to the behavior of these solutions against *S. aureus*. The initial studies showed that the addition of skim milk to Roccal had much less effect with this organism than with *E. coli*. With the glass slide technique no potentiating effect was observed with concentrations of skim milk between 0.02 and 1.0%. Since even 1% had little effect upon germicidal activity, higher concentrations were included in subsequent tests, in which both glass slide and plating methods were employed (Table II). Although the number of organisms subjected to germicidal action was proportionately much greater in the plating technique, and the concentration of Roccal was only one-fifth of that in the glass slide tests, the percentage survival, except in the presence of the higher concentrations of skim milk, was significantly lower. Nevertheless, both methods agree in indicating that the presence of skim milk in fairly high concentrations has little effect upon the ability of Roccal to destroy *S. aureus*. Having established this point, a further series of comparisons between Roccal and the hypochlorite was

TABLE II

EFFECT OF ADDED SKIM MILK ON GERMICIDAL EFFICIENCY OF ROCCAL IN DISTILLED WATER AS JUDGED BY PLATING AND GLASS SLIDE TECHNIQUES. *S. aureus*

% added skim milk	Plating (20 p.p.m.) ^a			Glass slide (100 p.p.m.) ^b		
	Count of survivors after exposure period, sec.			Count of survivors after exposure period, sec.		
	5	10	15	5	10	15
0.0	0	0	0	51	4	1
0.1	0	0	0	71	5	2
0.5	0	0	0	129	45	10
1.0	48	0	0	176	57	12
2.0	19	4	2	135	26	4
5.0	130	+	99	+	297	54
10.0	++	++	++	+	353	360
20.0	+++	+++	+++	++	+	+
50.0	++++	++++	++++	+++++	++++	+++

^a Germicidal solution contained 5,000,000 cells per ml. at start.

^b Estimated number of cells in film on glass slide at start, 200,000: 99.9% destruction would leave 200 cells.

carried out with both test organisms, using the glass slide technique. Concentrations of germicide were again selected to give approximately equal survival in the absence of added skim milk. The results (Table III) bring out several points. Against *S. aureus* Roccal at 100 p.p.m. was as effective as 200 p.p.m. of Dalglish, while in addition it retained its activity in the presence of far higher concentrations of skim milk. On the other hand, against *E. coli*, in the absence of added organic matter, 25 p.p.m. of Dalglish was as effective as 200 p.p.m. of Roccal. These findings concerning the relative potency of the two types of sanitizing agent in the absence of added organic matter agree with those recently published (9).

When the above concentrations of Roccal and Dalglish were compared against *E. coli* in the presence of more than 0.1% of added skim milk, Roccal appeared to better advantage. However, when further tests were run using 200 p.p.m. concentrations of both germicides, Dalglish was less sensitive to added skim milk than was Roccal (Table IV). Further tests with Dalglish showed good killing with 2% added skim milk, but with 5%, plates were uncountable.

Tests Using Tap Water

Mention was made earlier of the influence of the type of water used in preparing working dilutions of these germicides upon their activity. At this stage it was found that against *E. coli*, 50 p.p.m. of Roccal prepared with distilled water was roughly equivalent to 100 p.p.m. prepared with Ottawa tap water or to 200 p.p.m. prepared with a well water with a total hardness of 162 p.p.m. as calcium carbonate. Against *S. aureus* there was little difference. In the light of these findings, it was decided to repeat some of the

TABLE III

EFFECT OF ADDED SKIM MILK ON GERMICIDAL EFFICIENCY OF DISTILLED WATER SOLUTIONS OF ROCCAL AND DALGLISH. GLASS SLIDE TECHNIQUE

<i>S. aureus</i> ^a % added skim milk	Dalglish, 200 p.p.m.			Roccal, 100 p.p.m.		
	Count of survivors after exposure period, sec.			Count of survivors after exposure period, sec.		
	5	10	15	5	10	15
0.0	8	0	0	6	3	1
0.1	11	1	1	2	5	0
0.5	118	7	2	67	12	5
1.0	2800	1000	135	86	22	1
2.0	+++	+++	+++	160	68	23
5.0	++++	++++	++++	260	96	63
10.0	++++	++++	++++	458	238	80
20.0	++++	++++	++++	+	530	329

<i>E. coli</i> ^b % added skim milk	Dalglish, 25 p.p.m.			Roccal, 200 p.p.m.		
	Count of survivors after exposure period, sec.			Count of survivors after exposure period, sec.		
	5	10	15	5	10	15
0.0	14	3	5	37	3	2
0.1	162	9	3	94	5	3
0.2	1700	111	15	155	5	2
0.5	+++	+++	3000	1600	9	6
1.0	+++	+++	+++	++	2400	121
2.0	++++	++++	++++	+++	++	2100

^a 99.9% destruction leaves 105 colonies per slide.^b " " " 230 " " "

TABLE IV

EFFECT OF ADDED SKIM MILK UPON GERMICIDAL EFFICIENCY OF DISTILLED WATER SOLUTIONS OF ROCCAL AND DALGLISH. GLASS SLIDE TECHNIQUE. *E. coli*

% added skim milk	Dalglish, 200 p.p.m.			Roccal, 200 p.p.m.		
	Count of survivors after exposure period, sec.			Count of survivors after exposure period, sec.		
	5	10	15	5	10	15
0.0	13	9	4	47	30	12
0.1	15	13	4	43	17	16
0.2	12	12	7	264	38	38
0.5	37	43	27	+	29	17
1.0	20	21	18	++	+	278

N.B. 99.9% destruction leaves 190 colonies per slide.

TABLE V

EFFECT OF ADDED SKIM MILK WHEN SOLUTIONS PREPARED WITH TAP WATER.
ALL SOLUTIONS 100 P.P.M.

% added skim milk	<i>S. aureus</i> ^a						<i>E. coli</i> ^b					
	Count of survivors after exposure period, sec.						Count of survivors after exposure period, sec.					
	5	10	15	5	10	15	5	10	15	5	10	15
	Dalglish			Roccal			Dalglish			Roccal		
0.0	8	1	2	493	53	0	10	5	2	++++	++++	++++
0.1	8	1	1	448	8	2	17	4	3	++++	++++	++++
0.2	9	5	2	1320	38	7	65	7	4	++++	++++	++++
0.5	+++	+	214	+	212	8	615	248	214	++++	++++	++++
1.0	+++	+++	+++	++	+	91	+++	+++	+++	++++	++++	++++
2.0	+++	+++	+++	++	+	458	+++	+++	+++	++++	++++	++++
5.0				+++	+	857	+++	+++	+++	++++	++++	++++
10.0				+++	++	+						
20.0				+++	++	++						

^a 99.9% destruction leaves 232 colonies.

^b " " " 310 "

above work using solutions prepared from Ottawa tap water, which showed a hardness of 64 p.p.m. In the first set of tests, both test organisms were compared against tap water solutions of Roccal and Dalglish containing 100 p.p.m. respectively of active ingredient. Table V shows that a Roccal solution prepared from tap water destroyed *S. aureus* in the absence of organic matter nearly as quickly as a solution prepared from distilled water (Table III). However, with larger addenda of skim milk, the tap water solution was definitely less active. The tap water solution of Dalglish compared more favorably with the Roccal solution than when distilled water solutions were compared (Table III), although again beyond a certain concentration of added skim milk there was a more abrupt drop in activity than with Roccal.

Turning now to *E. coli*, a much greater difference in the behavior of the two germicides was noted than with the distilled water solutions (Table IV). All plates from Roccal-treated slides were uncountable, while Dalglish showed excellent germicidal activity with additions of up to 0.2% skim milk. Beyond 0.5%, however, the solutions were ineffective.

Since Roccal at 100 p.p.m. proved so ineffective against *E. coli*, similar tests were conducted using 200 p.p.m. solutions of each germicide. In addition, a further change was made. In previous studies, the required amount of skim milk had been added to all lots of germicidal solution before starting to measure the germicidal activity of the first solution. Subsequently, titrations of Dalglish solutions shortly after they had been used to treat the glass slides indicated a marked decline in strength with the higher concentrations of added skim milk. Consequently, in order to place all solutions on a more even footing in respect to initial strength, the procedure was

changed and the skim milk added to the test solution immediately before introducing the first glass slide for germicidal treatment. The results from these tests appear in Tables VI and VII. With *E. coli*, in order to be able to measure the effect of the added skim milk on the Roccal solution, longer exposure periods were employed with Roccal than with Dalglish. Surprisingly enough, the change in the time of adding the skim milk had less effect with Dalglish than was expected.

TABLE VI

EFFECT OF ADDING SKIM MILK IMMEDIATELY BEFORE TESTING WHEN SOLUTIONS PREPARED WITH TAP WATER. *E. coli*

% added skim milk	Dalglish, 200 p.p.m.			Roccal, 200 p.p.m.		
	Count of survivors after exposure period, sec.			Count of survivors after exposure period, sec.		
	5	10	15	10	20	30
0.0	4	1	3	++	564	39
0.1	11	10	4	++	213	40
0.2	4	4	3	++	206	112
0.5	5	3	1	++	+	392
1.0	6	4	1	+++	+++	++
2.0	48	123	199	+++	+++	++
5.0	++	+++	+++			

Solutions prepared 24 hr. before testing, then reinforced

0.1	12	5	2	840	13	6
0.2	1	5	2	+	21	13

N.B. 99.9% destruction leaves 310 colonies per slide.

While these results indicate that such concentrations of skim milk as might be picked up by sanitizing rinses do not interfere with the germicidal activity, it was deemed advisable to see whether this also held true where the solutions containing added skim milk were held for 24 hr. before testing. This would more nearly approximate the condition of a sanitizing rinse recovered after use and re-used the following day. Consequently, small amounts of skim milk were added to solutions of Roccal and Dalglish, then after 24 hr. at room temperature the strength of Dalglish was readjusted to the original concentration. (Roccal solutions showed no significant drop in strength when tested with the Universal Test Kit*, so they were not reinforced.) The results of one such test, shown in the lower part of Table VI, indicate no reduction in potency of Dalglish solution, while Roccal actually shows enhanced activity against *E. coli*. Results from similar tests with *S. aureus* appear in the lower section of Table VII. Here, instead of comparing the reinforced solutions of Dalglish against the freshly prepared solution of full strength, comparisons

* Obtained from Dr. Geo. J. Hucker, Geneva, N.Y.

TABLE VII

EFFECT OF ADDING SKIM MILK IMMEDIATELY BEFORE TESTING WHEN SOLUTIONS PREPARED WITH TAP WATER. *S. aureus*

% added skim milk	Dalglish, 200 p.p.m.			Roccal, 200 p.p.m.		
	Count of survivors after exposure period, sec.			Count of survivors after exposure period, sec.		
	5	10	15	5	10	15
0.0	3	1	1	49	2	1
0.1	1	2	1	47	1	0
0.2	4	0	1	35	1	0
0.5	3	2	1	61	0	0
1.0	21	2	1	129	8	0
2.0	17	8	4	570	413	94
5.0	+++	+++	+++	+	+	163
10.0				++	+	386
20.0				+++	++	637

Solutions prepared 24 hr. before testing, not reinforced

0.1 ^a	2	3	0	32	1	0
0.2 ^b	3	1	2	34	2	1

Solutions freshly prepared to match strength of 24 hr. old solutions

0.0 ^a	61	5	3			
0.0 ^b	26	9	4			

^a Dalglish solution 108 p.p.m.^b " " 42 "

N.B. 99.9% destruction leaves 385 colonies per slide.

were made between the unreinforced solutions and freshly prepared solutions of the same chlorine content. The results again indicate no reduction in the potency of either sanitizing agent as a result of adding skim milk. Similar results were obtained starting with 100 p.p.m. solutions of both germicides, and using either whole or skim milk addenda.

In an endeavor to discover the reason for the discrepancy between these results and those of Mallmann and Edwards (11), an attempt was made to duplicate their experiment. However, when a tap water solution of Dalglish containing 20 p.p.m. available chlorine plus 0.2% skim milk was held for 24 hr. at room temperature in the dark, the chlorine was entirely dissipated. The greater loss here than that reported by the above workers was doubtless due to the higher pH value of our solution (9.88 for 100 p.p.m.) compared with their chlorine water solution. As Wright (16) and Prucha (13) have shown, increased alkalinity hastens the loss of chlorine in the presence of organic matter.

Further tests were run using Dalglish tap and distilled water solutions of varying original strengths, held for 24 hr. after adding skim milk, comparing against freshly prepared solutions of equivalent available chlorine concentration. The results appear in Tables VIII and IX. They show that a 'used' solution titrating 12 or 13 p.p.m. available chlorine was far less active than a freshly prepared one showing the same strength by titration; at 30 to 35 p.p.m., the difference was slight, and at 100 p.p.m. it had disappeared.

TABLE VIII

GERMICIDAL EFFICIENCY OF 'USED' HYPOCHLORITE SOLUTIONS VS. *S. aureus*.
GLASS SLIDE TECHNIQUE

Solution	% added skim milk	P.p.m. Av. Cl		Count of survivors after exposure period, sec.					
		As prepared	As used	2	5	10	20	40	60
A ^a	0.1	40	12		++++	+++	+++	++	+
B ^a	0.0	13	13		210	32	33	9	7
A ^a	0.1	50	12.5		++++	+++	+++	++	+
B ^a	0.0	12.5	12.5		19	7	3	6	1
C ^b	0.1	50	7.3		++++	++++	+++	+++	++
A ^b	0.1	100	34	++++	+++	146			
B ^b	0.0	32	32	++++	+++	32			
C ^b	0.1 ^c	100	30	++++	+++	41			
D ^b	0.0	50	50	455	13	9			
E ^b	0.1	50	50	1150	28	5			
F ^b	0.2	50	50	++	160	16			
A ^b	0.1	200	108	49	6	3			
B ^b	0.0	105	105	45	11	4			
C ^b	0.2	200	38	+++	89	27			
D ^b	0.0	194	194	23	1	1			

^a Prepared with distilled water.

^b " " tap "

^c Whole milk addendum.

Solutions A and C held with added skim milk for 24 hr. at room temperature before testing; remainder prepared immediately prior to testing.

Practical Tests with 'Used' Solutions

To determine whether the slight potentiating action of small addenda of skim milk observed with the glass slide technique would show up under practical conditions, tests were made using two small (50 gal.) coil pasteurizing vats. Various procedures were tried before the following was adopted. The vats were sterilized with steam, then after cooling sprayed with skim milk containing between two and five million cells of the test organism per milliliter. The vats were allowed to stand overnight with the lids closed, so that the film of skim milk would dry onto the walls. Next morning an area of 1 sq. ft. on each vat was swabbed with a moist cotton swab, the stick cut,

TABLE IX

GERMICIDAL EFFICIENCY OF 'USED' HYPOCHLORITE SOLUTIONS VS. *E. coli*.
GLASS SLIDE TECHNIQUE

Solution	% added skim milk	P.p.m. Av. Cl		Count of survivors after exposure period, sec.					
		As prepared	As used	2	5	10	20	40	60
A ^a	0.1	40	12		++++	+++	+++	++	+
B ^a	0.0	13	13		30	24	19	16	8
A ^a	0.1	50	12.5		++++	+++	+++	++	++
B ^a	0.0	12.5	12.5		25	9	25	2	3
A ^b	0.1	100	34	++	65	6			
B ^b	0.0	34.5	34.5	111	10	7			
C ^b	0.1 ^c	100	35	65	9	5			
D ^b	0.0	50	50	15	7	3			
E ^b	0.1	50	50	44	27	5			
F ^b	0.2	50	50	107	19	4			
A ^b	0.1	200	108	5	2	3			
B ^b	0.0	105	105	6	2	2			
C ^b	0.2	200	38	192	16	5			
D ^b	0.0	194	194	12	3	2			

^a Prepared with distilled water.^b " " tap "^c Whole milk addendum.

Solutions A and C held with added skim milk for 24 hr. at room temperature before testing; remainder prepared immediately prior to testing.

and the cotton dropped into a dilution blank containing 99 ml. of sterile physiological saline. After shaking for one minute, plates were prepared and incubated at 32° C. for 48 hr.

One vat was then sprayed with Dalglish solution made up to 100 or 200 p.p.m. available chlorine the previous day, at which time 0.1% of skim milk had been added. After holding overnight in the dark at room temperature this solution was reinforced to its original strength, while a solution freshly prepared to match the titratable chlorine content was used to spray the other vat. A different area was swabbed immediately after the spraying, and a third area two hours later to determine the residual effect. Plates were prepared from each swab the same as for the control swabs. *S. aureus* and *E. coli* were again used as test organisms.

The results from several tests are given in Table X. Here there is no evidence of a reduction in sterilizing effectiveness where the 'used' hypochlorite solution, which had stood overnight at room temperature, was reinforced to its original strength. On the contrary, in every instance the 'used' solution was more effective than the fresh. Nor did the fact that the organisms suspended in skim milk had been sprayed on the vat walls appear to have had any effect. (In the earlier tests, suspensions of the test organism in 10%

TABLE X

EFFECTIVENESS OF FRESH VS. 'USED' HYPOCHLORITE SOLUTIONS IN SANITIZING PASTEURIZING VATS

	Available chlorine, p.p.m.			Control area plate count per square foot ^a	Treated area, % survival after spraying			
	Freshly prepared	'Used'			Swabbed immediately		Swabbed after 2 hrs.	
		Before reinforcement	After reinforcement		A ^b	B ^b	A ^b	B ^b
<i>S. aureus</i>	200	125	200	9,200 ^c	—	2.0	7.2	5.5
	99	34	96	290,000	4.4	0.34	0.82	0.06
	100	32	100	1,500,000	1.56	0.0004	<0.016	<0.0004
<i>E. coli</i>	205	116	198	350,000	0.16	0.05	0.32	0.09
	97	12	100	2,300,000	0.87	0.23	1.22	0.48

^a Average of swabbed areas of both vats.^b A—Solutions freshly prepared. B—Solutions containing 0.1% skim milk prepared the previous day and reinforced to original strength before using.^c Vats hosed down with cold water two hours after spraying with skim milk suspension of test organism.

skim milk were used; in addition, the vats were rinsed down with clear cold water two hours after being sprayed with the test organisms. However, where this was done, the number of organisms present after the sanitizing treatment was so small that satisfactory counts could not be obtained). Despite the fact that the test organisms were present in the skim milk layer on the walls of the vat, the percentage reduction in count as a result of spraying with the hypochlorite solutions was very gratifying. The data also suggest a continuing germicidal activity against *S. aureus* on the part of the residual hypochlorite during the two hour period subsequent to the sanitizing treatment.

Discussion

An interesting feature of these studies has been the finding that small concentrations of skim milk, such as might be picked up by a sanitizing rinse, not only fail to depress the germicidal activity of the two germicides employed, but frequently cause a slight enhancement of activity against both test organisms. This is decidedly at variance with the popular concept of the effect of added organic matter upon germicidal activity, particularly with hypochlorites, and is in marked contrast to the results reported by Mallmann and Edwards (11).

The effect of organic matter upon the germicidal activity of hypochlorite solutions appears to depend very largely upon the strength of the solution at the time of use. As will be seen from the data in Tables VIII and IX a 'used' hypochlorite solution titrating 12 or 13 p.p.m. available chlorine had far less germicidal power than a fresh one showing the same strength by titration. At 30 to 35 p.p.m. the differences were slight, while at 100 p.p.m. they had disappeared. These results help resolve the contradiction between

the findings of Mallmann and Edwards and our own. Had they started with solutions of the strengths commonly used in milk plants (50 to 200 p.p.m. available chlorine), they would doubtless have reached different conclusions concerning the germicidal activity of 'used' hypochlorite solutions.

The importance of thoroughly cleaning the surfaces of food handling equipment before attempting a sanitizing treatment has been universally stressed. Even though our results fail to show the expected reduction in germicidal activity of hypochlorites and quaternary ammonium compounds in the presence of added skim or whole milk, it cannot be overemphasized that this must not be interpreted as meaning that thorough cleaning of equipment is unimportant. Where milk or other food residue is allowed to remain, unsightly films build up which interfere with heat transfer while protecting resistant types of bacteria. The large numbers of thermophilic organisms found in milk that has been handled in milking utensils coated with milk-stone (a sure indication of faulty cleaning procedure) are an indication of what may be expected where cleaning is inadequate.

The slight potentiating effect of small addenda of skim milk upon the germicidal activity of Roccal and Dalglish solutions is in line with our findings previously reported (9) that skim milk increased the bacteriostatic and bactericidal effect of quaternary ammonium compounds in the glass slide technique. However, the explanation advanced at that time (absorption and carry-over of larger amounts of the germicide on the film of milk) is inadequate in this case. Wolf and Cousins (15), discussing their findings that vegetative cells dried in a milk film on a metal surface show optimum 'kills' at much higher pH values than was expected, postulate a reaction between the hypochlorite and the protein film to form a 'chloroamine', which is more germicidal than hypochlorite at pH values above 9.5. Even assuming that a similar reaction takes place with the glass slide technique, this fails to explain why the presence of additional small amounts of skim milk in the germicidal solution itself appears to increase its activity.

The influence of the type of water used in diluting the germicides on the susceptibility of the two test organisms was quite striking. (Further studies on this phase of the work will be reported separately.) While Roccal solution prepared with distilled water was appreciably more effective against *S. aureus* than against *E. coli*, the difference was slight compared to that shown by solutions prepared with tap water. Since the quaternary ammonium compounds usually become more effective with increasing pH (2, 5, 6, 9), while here the reverse holds true, some factor other than pH is evidently involved. The hypochlorite, on the other hand, was slightly more effective in tap water solution, presumably on account of the lower pH of the solution (4, 7) resulting from the buffering action of the tap water.

Both germicides retained a surprisingly high degree of effectiveness in the presence of considerable concentrations of skim milk. Roccal showed a gradual decline in effectiveness with increasing amounts of organic matter, whereas the hypochlorite showed a sudden drop.

It will be observed that the plating technique shows a much greater reduction in bacterial numbers than does the glass slide technique. That organisms freely suspended in the germicide solution would be more easily killed than those present on a surface in a film of skim milk is to be expected. In addition, the clumping of bacteria in quaternary ammonium solutions, as reported by McCulloch (12), may be a factor in lowering the plate count of survivors. A technique in which the organisms are present on a surface is therefore likely to yield results more representative of those obtained in the actual sanitizing of surfaces of food handling equipment.

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Addendum

Since this paper was prepared, Neave and Hoy (J. Dairy Res. 15 : 24-54. 1947.) have reported that the addition of 0.2% of whole milk to a hypochlorite solution containing 200 p.p.m. available chlorine had no significant effect upon the destruction of *S. aureus*. Their statement that "If the milk had remained in contact for a longer period and more tests had been made, there is no doubt that a significant decrease in germicidal power would have been shown" does not appear to have been substantiated by our results. They also refer to the work of Bryan *et al.* (J. Milk Tech. 5 : 77-85. 1942.), which indicated that the addition of 5% milk to hypochlorite solutions containing 40 to 200 p.p.m. available chlorine greatly lowered the germicidal efficiency against mastitis streptococci.

CHEMICAL AND MICROBIOLOGICAL STUDIES ON STORED, SALTED BUTTER¹

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Abstract

Salted butter from two Canadian plants was stored in parchment wrappers and in cans at -1.1° , 10.1° , 21.1° , and 32.2° C. (30° , 50° , 70° , and 90° F.). Deterioration of the stored samples was followed by assessment of flavor, and by determination of: total acidity, free acidity, amino acid, pH, and fluorescence of the butter serum; peroxide oxygen, free fatty acids, and fluorescence of the butterfat; acidity of the whole butter; the number of viable, proteolytic, lipolytic, and oxidase positive organisms; and yeast and mold counts.

Butter in cans deteriorated less rapidly than print samples although differences were less pronounced at 70° and 90° F. than at 30° and 50° F. Canned samples did not change appreciably in quality during 45 weeks' storage at 30° F. In general, decomposition of the serum and flavor deterioration became evident before changes occurred in the fat fraction. Stability of the serum was the limiting factor in keeping quality. The formation of amino acids and intermediate products of protein decomposition contributed largely to flavor changes.

Flavor scores were more closely related to chemical objective test values than to microbiological counts. Storage temperature showed a marked influence on the correlation of objective test values with flavor score. Of the objective tests studied, total serum acidity (amino acidity plus free serum acidity) pH and serum fluorescence were most closely associated with flavor score.

Introduction

The production of butter is seasonal and is usually concentrated in areas where fluid milk is not readily marketed. These factors emphasize the importance of keeping quality if butter is to reach the consumer in good condition. Many studies have been made to improve methods of handling the cream and of packaging butter. It has been reported that butter develops tainted flavors when stored in wooden containers (8, 11, 18). Partial success in preventing the production of these flavors by the use of various types of liners has been reported (2, 3, 17).

Butter has been shipped to countries in the tropics for many years, often arriving in poor condition, and consumers there have become conditioned to using a product that is undesirable by temperate zone standards. This state of affairs is accepted as inevitable by consumers and exporters alike, and no particular effort has been made to improve the quality of canned butter for export. During the war, canned butter was included in Red Cross parcels and in special service rations. In an effort to extend the storage life of butter for these purposes, greater attention than heretofore was given to initial quality.

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The information available about keeping quality is contradictory and relates chiefly to studies of accelerated shelf tests. This investigation was carried out to obtain factual data on changes in butter at storage temperatures above those used in warehouses (i.e. -10° to 0° F.). As butter contains more than one component, it is logical that storage temperature may affect one component more than another and thus deterioration may be favored in specific fractions at different temperatures. Therefore, the butter was stored over a range of temperatures to try to establish the relative susceptibility of different components at high and low temperatures.

Many factors have been suggested as responsible for spoilage in butter, and it was felt that no one test would satisfactorily assess keeping quality. Although organoleptic tests measure the over-all quality of butter, they lack uniformity between investigators. Therefore, a number of chemical and microbiological determinations were carried out on whole butter, butter serum, and butterfat from stored whole butter.

The present study compares the keeping quality of canned and print butter over a wide range of temperatures using a number of chemical and microbiological methods. The degree of association between the results of these methods and organoleptic assessment was also determined.

Experimental

The experimental material consisted of two lots of commercial first grade Canadian salted butter prepared from pasteurized cream. One lot was selected from a single churning of Western butter and the second was prepared from selected neutralized cream in an Eastern creamery. Part of the latter lot was canned immediately in lacquered cans without parchment wrapping and an equal part prepared in parchment-wrapped 2-lb. prints. The Western butter churning was selected on the basis of low yeast and mold counts and an accelerated storage test. Cylindrical 1-lb. prints were then prepared and wrapped in parchment; half of these were sealed in lacquered cans. All the material was shipped by refrigerated car to Ottawa and held at -40° F. until allotted at random to experimental conditions.

The canned and the print butter from both plants were stored at 30° , 50° , 70° , and 90° F. The prints were stored in sterile beakers covered with brown wrapping paper. Samples were withdrawn at intervals depending on storage temperature: at 30° F., after 16, 32, 64, 128, 192, 256, 321, and 385 days; at 50° F., after 4, 8, 16, 32, 64, 96, 128, 192, and 256 days; at 70° F., after $\frac{1}{2}$, 1, 2, 3, 4, 8, 16, 32, 64, and 128 days; and at 90° F., after $\frac{1}{2}$, $\frac{1}{2}$, 1, 2, 3, 4, 8, 16, and 32 days.

Methods

A quantitative determination by chemical methods of the substances causing off-flavors in butter is difficult, because of the complexity of the reactions accompanying spoilage. However, chemical and microbiological methods are undoubtedly of value for comparison of similarly treated products.

The following objective measurements were selected for study: peroxide oxygen, free fatty acid, Kreis value, and fluorescence of the fat fraction; acidity of whole butter; amino acid by Sorensen's titration, and acidity and fluorescence of the butter serum. Viable, lipolytic, proteolytic, and oxidase positive organisms; and yeast and mold counts on the whole butter were also included.

Preparation of the Sample for Analysis

Samples for microbiological examination were taken first with sterile cork borers, made of stainless steel. The butter stored at 90° F. was very soft, necessitating cooling for a few hours at 45° F. When time did not permit hardening by cooling, the wrapper was removed, the sample mixed, and representative portions taken with a sterile tongue depressor. The square prints were sampled through the face opposite to that on which the parchment flaps met. With the round prints, borings were taken through the face just past the paper overlap. The cans were flamed on top and opened with a wheel-type can opener that had been flamed. The lid and cover paper were removed and borings taken at and around the center. Enough material was taken from the cans and prints to give at least 20-ml. portions when melted. Samples of whole butter were withdrawn for immediate organoleptic rating and whole butter acidity measurements.

Serum and fat were separated by a method previously described (10). Briefly, the butter is heated in centrifuge bottles placed on a steam bath at 212° F., stirred (with a thermometer) until it reaches 110° to 120° F., then centrifuged for 10 min. at 1700 r.p.m. The fat is removed by siphoning and filtering through absorbent cotton, and part of the clear portion of the serum is pipetted into a separate container.

Organoleptic Ratings

Two sets of organoleptic ratings were obtained. The butter was scored for flavor only by three professional graders, by methods outlined in the Canadian Dairy Industry Act and Regulations, 1942, pp. 48 to 51. The second system, which permitted statistical computations, employed a panel of 10 judges to assess flavor as follows: 10, excellent; 8, good; 6, fair; 4, poor; 2, bad; 0, unapproachable. At any one time the 10 tasters were required to score a set of four samples chilled to approximately 50° F.

Acids

The free fatty acids of the butter fat were determined by titrating 10 gm. dissolved in 50 ml. of hot ethanol with 0.02*N* sodium hydroxide, until neutral to phenolphthalein. This procedure was also used to determine acidity of the whole butter, which includes other titratable acids formed from protein and carbohydrate breakdown. A colorimetric method (13) was tried but proved to be inadequate.

A difference in amino nitrogen, as determined by Van Slyke's method (19, 20), was obtained between serums of fresh and spoiled butter, (0.073 mgm. of amino nitrogen per ml. of serum for fresh butter, 0.159 mgm. for

spoiled butter). This finding with the evidence of other investigators (15) suggested that protein deterioration was taking place. The acidity of the serum due to free acids, such as lactic, was determined by titrating an aliquot with 0.02 *N* sodium hydroxide, employing phenolphthalein as an indicator. The values are reported as mgm. of sodium hydroxide per 100 ml. of serum, and are termed free serum acidity. To obtain an estimate of the protein decomposition, the formation of amino acids was followed by Sorensen's titration. Although this method has its limitations, it enabled comparison between samples. The values are reported as mgm. of sodium hydroxide per 100 ml. of serum and are termed amino acids.

To estimate the over-all change in the serum, the values for free serum acidity and amino acids were combined and termed total serum acidity.

The hydrogen ion concentration of the serum was determined at 77° F. on 10 ml. of the serum by means of a pH meter.

Fluorescence

Since many types of fat show changes in fluorescence with storage (16), it was considered desirable to examine the change in the fat from stored butter. One-gram samples of butterfat from fresh and spoiled butter were dissolved in 10 ml. portions of solvents and their fluorescence measured on a Coleman photofluorometer with filters transmitting light in the region of 365 μ . The fluorescence readings are given in Table I. Of the solvents used, benzene

TABLE I
FLUORESCENCE OF BUTTERFAT DISSOLVED IN ORGANIC SOLVENTS

Solvent	Fresh butter	Spoiled butter	Difference
Benzene	64.5	41.0	23.5
Xylene	58.5	37.0	17.5
Dioxane	51.5	38.0	13.5
Ethyl ether	30.0	22.5	7.5
Ethylene dichloride	37.5	31.0	6.5
Amyl acetate	32.0	26.0	6.0
Petroleum ether	39.5	34.0	5.5
Acetone	15.5	17.5	2.0
Chloroform	21.5	20.0	1.5
Carbon tetrachloride	6.5	8.0	1.5
Ethanol	Too turbid	—	—
Methanol	Too turbid	—	—

and xylene resulted in the largest difference between fresh and rancid fat. Xylene was selected for further study. The effect of fat concentration was also investigated. The results in Table II indicate that the fluorescence of butterfat from fresh and spoiled butter increased with fat concentration, and also that the differences between fresh and spoiled butter were larger at the higher concentrations. As the differences between the spoiled and fresh butter were not the same at all concentrations tested, a standard concentration of

10% butter fat was chosen. However, as the test was not totally satisfactory, it was applied only to a limited number of samples. Serum fluorescence was determined as described previously (10).

TABLE II
THE EFFECT OF BUTTERFAT CONCENTRATION IN XYLENE ON FLUORESCENCE VALUES

Percentage of butterfat	Fresh	Spoiled	Difference
10	62.0	45.0	17.0
20	85.5	64.0	21.5
30	96.0	74.0	22.0

Peroxide Oxygen

Both the ferrometric and iodometric methods (5, 7) were employed for the estimation of peroxide oxygen value, for reasons outlined in a recent investigation on lard (9).

Kreis test

The modification by Walters *et al.* (21) of the original Kreis test (14) was selected as the most suitable because of its simplicity and development of color in a single phase system. Investigation by White (22) showed that the color intensity was proportional to the concentration of fat. One gram of butter oil was employed in each test. If the intensity of color after the reaction was too great, a dilution with solvent was made. The Evelyn photoelectric colorimeter (6) provided with a 580 Rubicon filter was found to be quite satisfactory for measurement of color intensity. The results are reported as modified extinction coefficients. Although the values obtained have little theoretical significance, they are quite suitable for comparison between samples.

Microbiological Methods

Samples were held at 40° F. until they could be plated. They were then melted at 110° F. and 10 ml. pipetted into a 90 ml. water blank preheated to 110° F. Appropriate dilutions were made in the blanks.

Viable counts were made on tryptone glucose agar with 0.5% skim milk added (1, p. 22). Both proteolytic (caseinolytic) and viable organisms were estimated on these plates, counts being made at two and three days after incubation at 90° F. and three and five days at 70° F. Yeasts and molds were estimated on Difco potato dextrose agar adjusted to pH 3.5 to 4.0 just before use. Counts were made after three and five days at 70° F. For the estimation of lipolytic organisms, butterfat was prepared from butter having a low free fatty acid content and no iodometric peroxide oxygen value and stained with neutral red base (12). Five per cent of stained fat was added to 2% agar containing 0.5% each of Difco proteose-peptone and tryptone.

Only colonies imparting a distinct red color to the fat globules under or around them were considered lipolytic. Oxidase positive organisms were detected on the same medium by using unstained fat and flooding the plates with a weak solution of dimethylparaphenylenediamine. Both lipolytic and oxidase positive organisms were counted after five days at 90° F. and seven days at 70° F.

Treatment of Data

The many data required statistical analyses to assess the relative importance of the factors involved. Each test is reported first from the standpoint of treatment effects. These effects are shown in detail in graphical form in Figs. 1 to 4, in which the results from the two plants are averaged, as it was more desirable to emphasize differences due to temperature and packaging than those due to source. The relation of chemical tests to flavor, and their assessment of keeping quality, are indicated by correlation and regression coefficients and an analysis of covariance (Tables IV to VI).

Results

Flavor

The mean flavor scores as assessed by the laboratory flavor panel are shown in Fig. 1. An increase in storage temperature or time caused a decrease in flavor score. The flavor score of the print butter decreased more rapidly than did that of canned butter at all the storage temperatures. There was only a slight decrease in flavor score of the canned butter after storage for 45 weeks at 30° F. At 50° F., the canned butter decreased in the first 14 weeks, then showed a definite improvement.

Further details of flavor results obtained by the butter graders and laboratory flavor panel are given in Appendix Tables I and II. For the purpose of this investigation the laboratory flavor assessment system was superior to that employed commercially as it could be correlated more easily with objective tests and furnished a more reliable assessment of the butter flavor by employing a larger group of tasters and a scoring system with equal increments.

Fluorescence

An increase in storage time or storage temperature resulted in an increased serum fluorescence value (Fig. 1). The rate of increase in the fluorescence was greater at 70° and 90° F. than at 30° and 50° F. The print butter showed a greater increase in serum fluorescence values at all the storage temperatures than that stored in cans. The canned butter stored at 30° and 50° F. showed approximately six units increase in serum fluorescence in 45 weeks.

As the fluorescence determinations on the fat fraction were not very informative, only a few examples are given in Table III. The fluorescence of the fat fraction did not change appreciably with flavor deterioration at any of the storage temperatures.

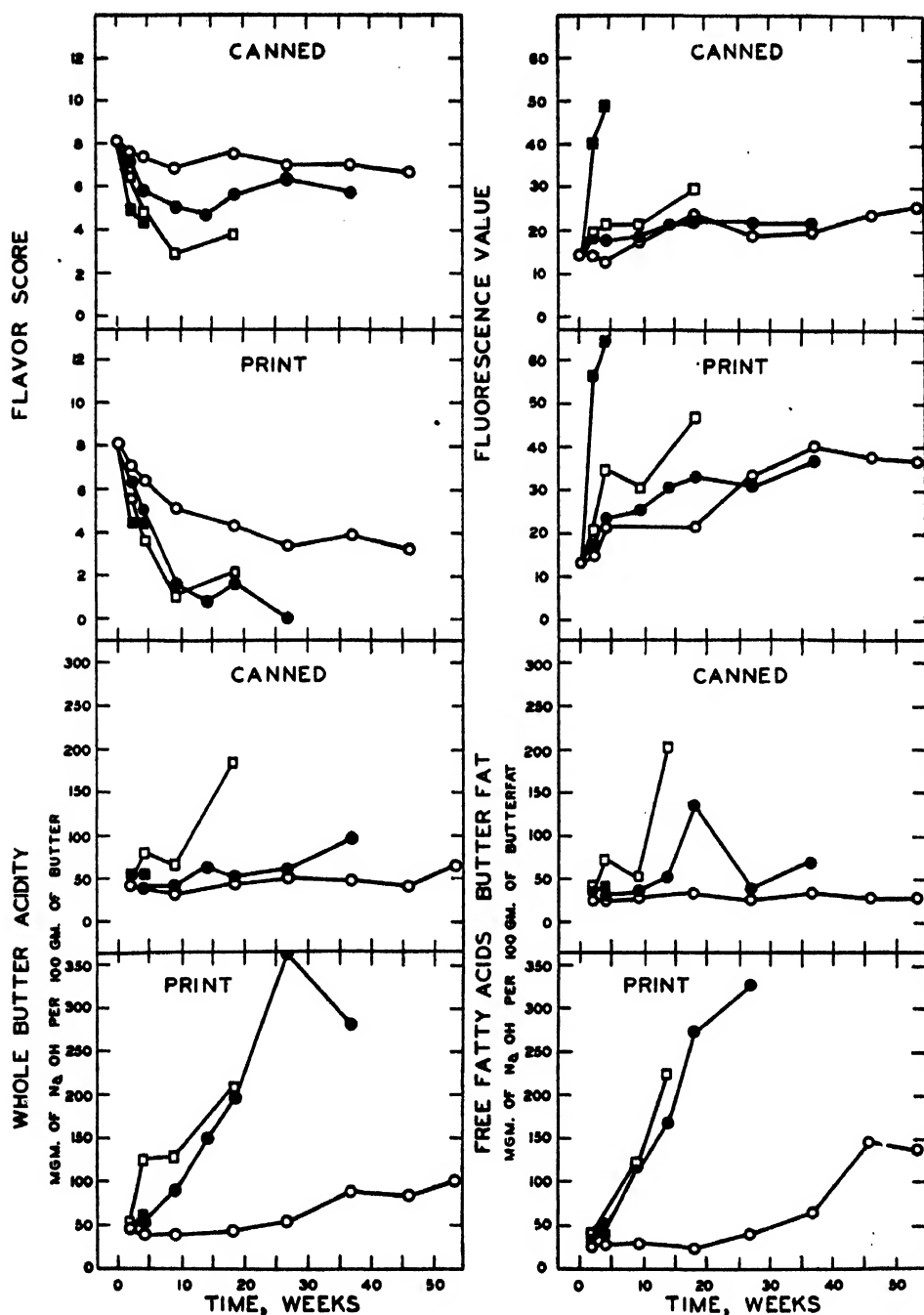


FIG. 1. Effects of storage at 30°, 50°, 70°, and 90° F. on the laboratory flavor panel score, serum fluorescence, whole butter acidity, and the free fatty acid content of butterfat from canned and print, salted butter. 30° F., ○; 50° F., ●; 70° F., □; 90° F., ■.

TABLE III

FLAVOR SCORES AND CHEMICAL MEASUREMENTS ON THE FAT FRACTION FROM BUTTER STORED AT 30°, 50°, 70°, AND 90° F.

(Values averaged over both plants and both packages)

Storage Temperature, °F.	Flavor score	Peroxide oxygen content		Kreis value	Fluorescence value
		Ferrometric	Iodometric		
90	8.1	0.0	0	0.3	60
	4.7	3.8	0	0.6	57
	4.4	1.7	0	0.7	56
70	8.1	0.0	0	0.3	60
	6.0	3.7	0	0.5	55
	4.2	1.5	0	0.6	57
	2.0	2.0	0	2.0	56
50	8.1	0.0	0	0.3	60
	6.8	2.8	0	0.4	56
	5.4	1.3	0	0.5	58
	3.3	1.6	0	0.3	56
	3.2	2.2	0.3	8.2	58
	2.8	5.1	1.3	6.5	—
30	8.1	0.0	0	0.3	60
	7.3	2.7	0	0.4	—
	6.8	1.8	0	0.4	55
	7.5	1.4	0	—	58
	7.0	2.5	0	—	56
	6.8	1.6	0	4.0	—
	5.8	—	0	—	—

Acids

The acidity determinations on the whole butter generally showed an increase with storage time and storage temperature for both canned and print wrapped butter (Fig. 1). The increase was more pronounced for print than for canned butter. The formation of acidity was suppressed in the canned butter stored at 30° and 50° F., and as this measurement is some indication of the hydrolysis of protein and fat, it is inferred that canning the material retarded the rate of spoilage. The canned butter showed only a slight increase in acidity after storage for 45 weeks at 30° F.

The free fatty acid content of the butter fat increased with storage time and storage temperature for both canned and print material (Fig. 1). There was a more prominent increase in the free fatty acids in the butter stored in prints than that stored in cans. There was little change in free fatty acids in canned material even after storage at 30° F. for 45 weeks.

From Fig. 2 it may be seen that the free serum acidity increased with storage time, the rate varying with the storage temperature. The butter stored in prints showed a greater rate of increase at all the storage temperatures. The butter stored at 30° F. in cans showed very little increase after 45 weeks, while that stored in the prints showed a substantial increase after 20 weeks.

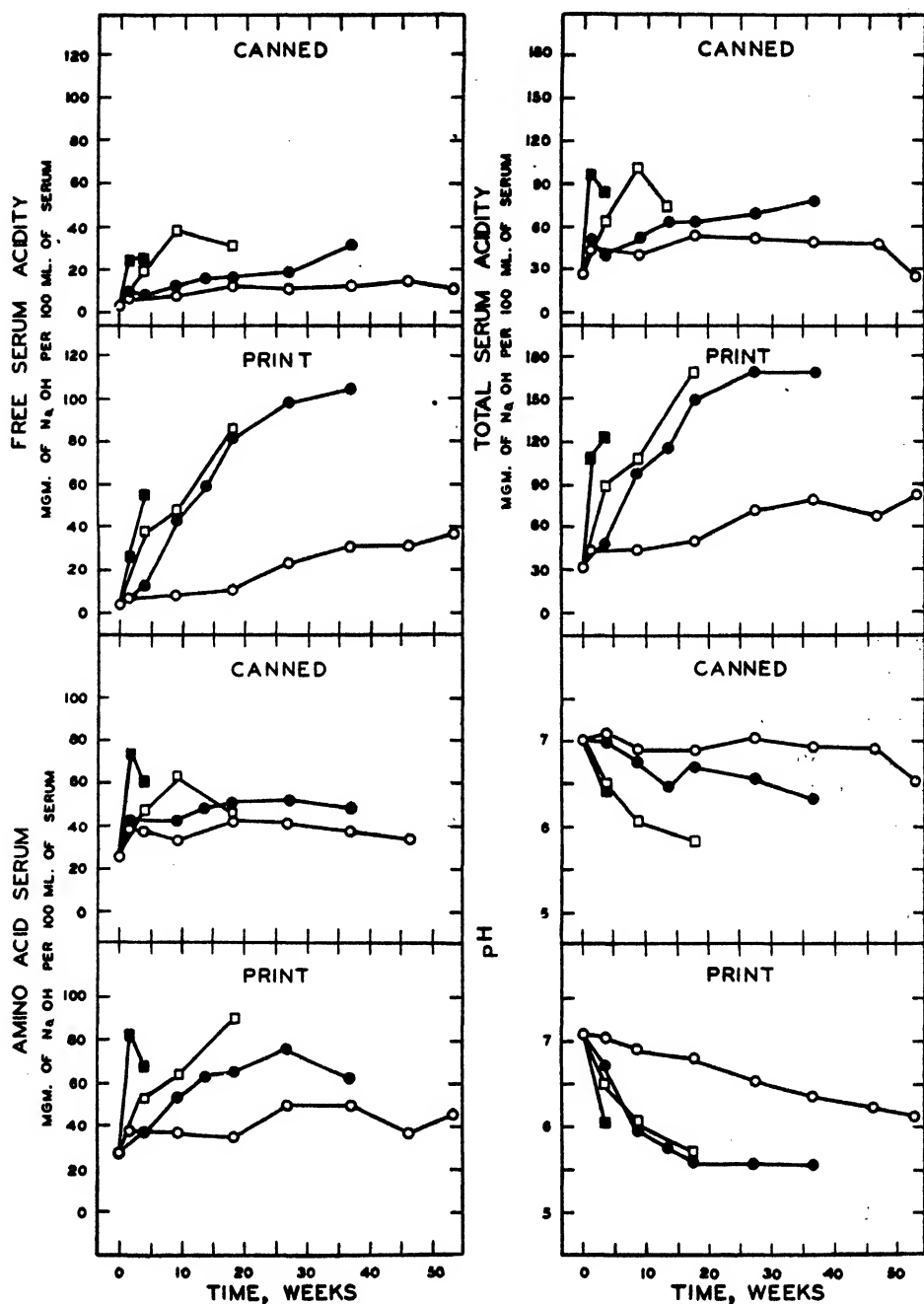


FIG. 2. Effects of storage at 30°, 50°, 70°, and 90° F. on free serum acidity, amino acid in the serum, total serum acidity, and pH of the serum from canned and print, salted butter. 30° F., ○; 50° F., ●; 70° F., □; 90° F., ■.

Canning of the butter appeared to suppress the formation of free serum acidity most at 30° and 50° F.

The amino acids showed an increase followed by a decrease with storage time (Fig. 2). This was accentuated at the higher storage temperatures. The rate of increase in the amino acids was greater at 70° and 90° F. than at 30° and 50° F. At all the storage temperatures the amino acid content developed somewhat more rapidly in the print butter than in the canned butter. The canned material stored at 30° F. showed little change after the first two weeks.

Increases in total serum acidity with period of treatment for both canned and print butter at all the storage temperatures may be seen from Fig. 2. In some cases, there was first an increase, then a decrease after prolonged storage. This was quite evident in butter stored in cans at 70° and 90° F. At all storage temperatures, print butter showed larger increases in total serum acidity than canned butter. From this evidence, it is apparent that the over-all changes in the serum were greater for material stored in prints.

The hydrogen ion concentration of the butter serum decreased with storage time (Fig. 2), the decrease being more rapid at the higher storage temperatures. The changes in print butter were greater than those in canned material. As the pH is a function of the fermentation taking place, it is considered that very little deterioration from this source took place in the canned butter stored at 30° F. for 45 weeks.

Peroxide Oxygen Content, Kreis Value

The results of determinations on the fat fraction are shown in Table III. The peroxide content as measured by both methods showed no large increase with flavor deterioration at any of the storage temperatures. The aldehyde content as measured by Kreis value showed a slight increase with flavor deterioration at the lower temperatures. The lack of appreciable increases in peroxide oxygen content and aldehyde with flavor deterioration suggests that oxidative changes in the fat fraction contribute little to the flavor deterioration in stored salted butter.

Microbiological Tests

Since there was little difference in the counts after incubation at 70° and 90° F., averages were taken, and since differences between conditions of storage were of primary interest, the results for butter from both sources were also averaged for graphical presentation. Owing to sampling errors, the bacteriological estimations show considerable variation. However, the data presented in Figs. 3 and 4 show the trends found at various storage temperatures.

The original number of both the viable and proteolytic organisms was slightly greater in the canned than in the print butter. In the canned material, there was a small but rapid increase during the first two days at 70° and 90° F. The general trends with all types of organisms were very similar in butter

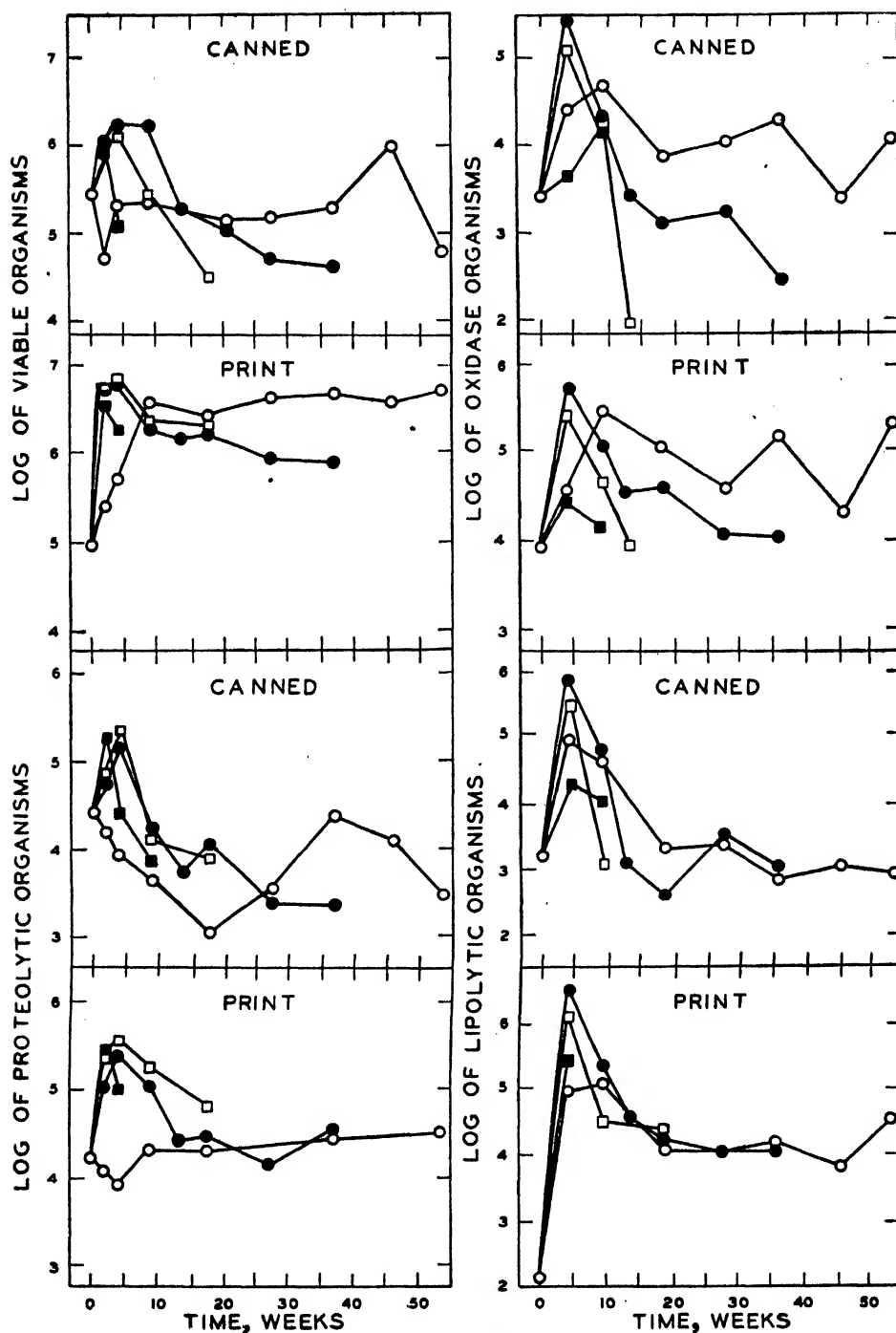


FIG. 3. Effects of storage at 30°, 50°, 70°, and 90° F. on viable, proteolytic, lipolytic, and oxidase positive organism contents of canned and print, salted butter. 30° F., ○; 50° F., ●; 70° F., □; 90° F., ■.

stored at 90° F. The number of bacteria reached a peak in three to four days, remained at approximately that level for 8 to 16 days, and then decreased. At 70° F., the peak came in four to eight days and the numbers remained fairly constant for 32 days. At 50° F. the increase was slower, the numbers

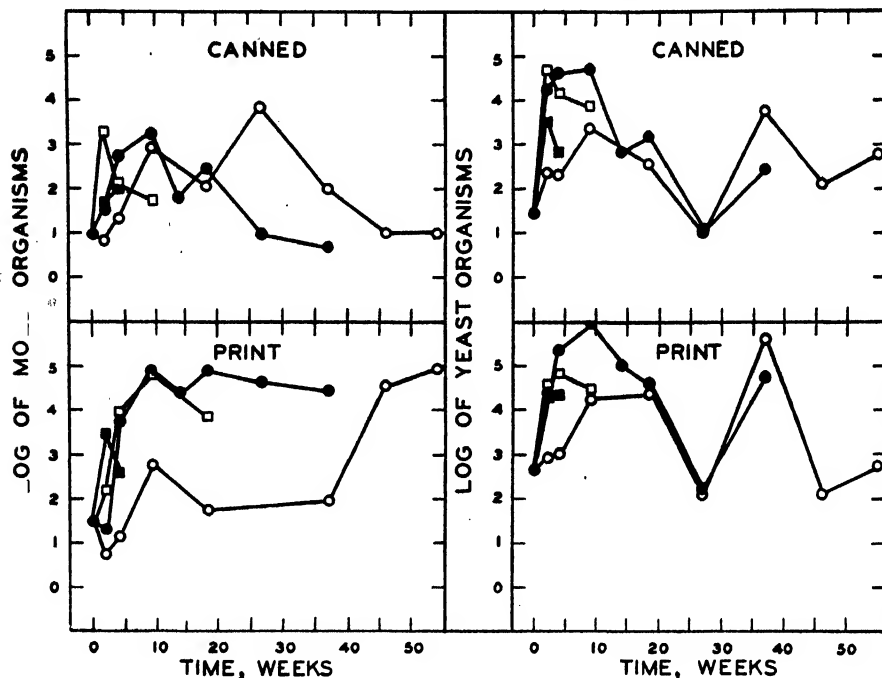


FIG. 4. Effects of storage at 30°, 50°, 70°, and 90° F. on mold and yeast organism contents of canned and print, salted butter. 30° F., ○; 50° F., ●; 70° F., □; 90° F., ■.

reaching a maximum in 16 to 32 days, and then decreasing after approximately 64 days. At 30° F., the trends were more uniform and the peaks were reached in from 32 to 70 days and in some cases even longer. In general, the changes in the canned butter were not so great as in the print and the organisms did not survive so long. In the prints, the number of organisms usually remained at a level as great as or greater than the original number, whereas in the canned butter the levels were usually below the original values.

The numbers of total viable organisms (Fig. 3) at both 70° and 90° F. rose rapidly, the increase in the prints being about 10 times greater than in the canned. In the butter stored at 50° F., the increase was more rapid in the prints and greater numbers were attained. At 30° F., there was little increase in the canned material, but in the prints the increase was decided and the number of organisms remained at a high level throughout the experiment.

The number of proteolytic organisms showed trends similar to those of the viable count (Fig. 3). At 30° F., there was very little increase. The decreases after the initial increases were somewhat steeper than for the total count.

The oxidase producing organisms increased at a much slower rate in the canned butter than in the prints (Fig. 3). However, in the canned material the numbers eventually decreased at the higher temperatures to levels equal to or lower than the original number. For the prints the decrease was slower, but counts finally reached the original level, except in the prints stored at 30° F.

Lipolytic organisms increased from a low original content of about 140 per gm. to about a million per gram in the print butter stored at 50° and 70° F. (Fig. 3). At the three lower storage temperatures, the average number remained at above 10,000 per gram for 20 weeks. In the cans the increase, although not great, was maintained over a similar period, and the number then dropped to approximately the original value.

The yeast count showed a greater increase in the canned butter than in the prints (Fig. 4). For both the print and canned butter stored at 30° F., there was a general increase for at least the first 35 weeks. The drop shown at the 27th week is due to a poor lot of media. Development of molds was much greater in the prints than in the canned material. This is readily seen from Fig. 4. The counts remained high in the prints, but in the canned butter there was some reduction after the first few weeks. Darkening of the surface due to molds was first noticed in the prints in 32 days at 70° F., in 64 days at 50° F., and in 192 days at 30° F. Light mold growth was noted a few times on the surface of the canned butter but never became distributed throughout the mass as in the prints.

Relation Between Flavor and Objective Test Values

The relation between flavor as assessed by the laboratory flavor panel and objective test values for each storage temperature was assessed by computing correlation and regression coefficients. An objective test, to be of value for general assessment of keeping quality, should have a correlation coefficient of at least .8 and there should be no significant difference in regression values between sets of data from material stored under different conditions. The significance of any difference in regression values for the butter stored at the four temperatures was determined by analysis of covariance.

The correlation coefficients of the relations between flavor and the objective tests are given in Table IV. All the objective test values increased with a decrease in the flavor score, except pH, which decreased. The chemical objective tests were more closely related to flavor changes than the bacteriological tests. The correlation coefficients between flavor and viable, proteolytic, oxidase, and yeast counts attained significance for storage at 30° and 90° F. while those for 50° and 70° F. were not significant. Lipolytic count correlated significantly with flavor only for 90° F. storage. Of all the bacteriological tests studied, the mold count gave the highest correlation coefficient with flavor and attained statistical significance for all temperatures except 30° F. Although the correlation coefficient between flavor and mold count was much higher than for the other bacteriological tests, they were still too

TABLE IV

SIMPLE COEFFICIENTS OF CORRELATION BETWEEN FLAVOR SCORES AND OBJECTIVE TEST VALUES FOR SALTED BUTTER STORED AT 30°, 50°, 70°, AND 90° F.

Quantities correlated:	30° F.		50° F.		70° F.		90° F.	
Flavor score with:	Degrees of freedom	r	Degrees of freedom	r	Degrees of freedom	r	Degrees of freedom	r
Viable count	29	-.56**	35	-.14	39	-.07	39	-.33*
Proteolytic count	28	-.36*	35	-.01	39	-.07	39	-.44**
Lipolytic count	29	-.27	35	-.10	38	-.12	39	-.46**
Oxidase positive count	29	-.45**	35	.01	39	-.23	39	-.34*
Yeast	29	-.59**	35	-.24	37	-.01	39	-.37*
Mold	29	-.30	35	-.84**	38	-.65**	39	-.36*
Butter acidity	30	-.59**	38	-.71**	41	-.79**	36	-.67**
Free fatty acids	30	-.61**	38	-.82**	41	-.71**	36	-.21
pH	30	.63**	38	.84**	41	.82**	36	.51**
Fluorescence	30	-.63*	38	-.69**	40	-.75**	36	-.84**
Amino acid	20	-.28	26	-.50**	22	-.61**	20	-.75**
Free serum acidity	20	-.75**	26	-.92**	22	-.67**	20	-.71**
Total serum acidity	20	-.82**	24	-.72**	26	-.86**	20	-.64**

* Indicates 5% level of statistical significance.

** Indicates 1% level of statistical significance.

low to predict flavor score with any degree of reliability. The whole butter acidity, free fatty acids, and pH showed higher correlation with flavor for the material stored at 50° and 70° F. than for that stored at 30° and 90° F. Correlation coefficients between flavor and serum fluorescence and amino acids increased with an increase in storage temperature. Of the chemical tests studied, free serum acidity and total serum acidity gave the highest correlation coefficients with flavor.

The regression coefficients between flavor and serum fluorescence, whole butter acidity, free fatty acids, free serum acidity, amino nitrogen, total serum

TABLE V

REGRESSION COEFFICIENTS BETWEEN FLAVOR SCORES AND OBJECTIVE TEST VALUES FOR SALTED BUTTER STORED AT 90°, 70°, 50°, AND 30° F.

Quantities correlated:	90° F.		70° F.		50° F.		30° F.	
Flavor score with:	Degrees of freedom	β	Degrees of freedom	β	Degrees of freedom	β	Degrees of freedom	β
Free fatty acids (whole butter)	36	-.087	41	-.027	38	-.017	30	-.058
Free fatty acids (butter fat)	36	-.019	41	-.021	38	-.016	30	-.054
pH on serum	36	1.35	41	2.94	38	3.49	30	2.70
Fluorescence value on serum	36	-.064	40	-.160	38	-.207	30	-.100
Amino nitrogen on serum	20	-.066	22	-.104	26	-.074	20	-.046
Free serum acidity value	20	-.060	22	-.073	26	-.061	20	-.132
Total serum acidity value	20	-.040	22	-.052	26	-.043	20	-.069

acidity, and pH on the serum for each storage temperature are given in Table V. It is quite evident that a difference in regression coefficients exists between the storage temperatures and the regression coefficients for pH are greater than for the other measurements. The significance of these differences was assessed by analysis of covariance (Table VI). No significant

TABLE VI

ANALYSIS OF COVARIANCE WITH STORAGE TEMPERATURES OF REGRESSION COEFFICIENTS
BETWEEN OBJECTIVE TESTS AND FLAVOR SCORE

Tests with flavor	Average regression coefficient		Individual coefficient		Difference in regression coefficients		Residual (pooled)	
	Degrees of freedom	Mean square	Degrees of freedom	Mean square	Degrees of freedom	Mean square	Degrees of freedom	Mean square
Fluorescence	1	235.42**	4	72.99**	3	18.85**	146	1.96
Free fatty acid (whole butter)	1	228.50**	4	67.23**	3	13.48**	138	1.90
Free fatty acid (butterfat)	1	242.36**	4	69.99**	3	8.53**	138	1.89
Free serum acidity	1	265.95**	4	69.78**	3	4.39	94	2.09
Amino nitrogen	1	127.19**	4	33.81**	3	2.68	94	3.65
Total serum acidity	1	263.60**	4	67.53**	3	2.16	94	2.18
pH on serum	1	334.39**	4	119.42**	3	47.77**	154	0.73

** Indicates 1% level of statistical significance.

difference in regression coefficients between storage temperatures was found for the relations between flavor score and free serum acidity, amino nitrogen, and total serum acidity. Significant differences between the storage temperatures were evident for the regression coefficients between flavor and whole butter acidity, free fatty acids, pH, and serum fluorescence.

Interrelation of the Chemical Measurements

The interrelation of the chemical measurements was assessed by computing correlation coefficients. The results are shown in Table VII. The fluorescence values were most highly associated over all the storage temperatures with amino acids and total serum acidity, and least with pH. From these results, it may be inferred that fluorescent materials are derived from amino acids or a reaction in which amino acids are involved. Free serum acidity and amino acids were not so closely associated as the amino acids and total serum acidity. This indicates that free serum acidity may be produced by microbiological action without significant production of amino acids. The pH was significantly correlated with all measurements but least so with amino acid content. A storage temperature of 30° F. gave a much lower association between the free fatty acids and other measurements except whole butter acidity. The acids content of the whole butter and butterfat were significantly correlated with the other measurements.

TABLE VII

SIMPLE CORRELATION COEFFICIENTS FOR THE INTERRELATION BETWEEN OBJECTIVE TESTS ON BUTTER STORED AT 30°, 50°, 70°, AND 90° F.

	Storage temp., °F.	Correlation coefficients					
		Butter acidity	Free fatty acids	pH	Amino acids	Free serum acidity	Total serum acidity
Fluorescence	90	.65**	.76**	-.21	.85**	.79**	.92**
	70	.82**	.90**	-.48**	.86**	.71**	.83**
	50	.70**	.77**	-.50**	.84**	.64**	.77**
	30	.70**	.72**	-.26	.67**	.59**	.79**
Total serum acidity	90	.87**	.93**	-.85**	.89**	.89**	
	70	.77**	.78**	-.76**	.88**	.95**	
	50	.82**	.90**	-.77**	.80**	.83**	
	30	.42*	.61**	-.27	.80	.77**	
Free serum acidity	90	.87**	.77**	-.84**	.58**		
	70	.75**	.81**	-.80**	.69**		
	50	.40	.91**	-.17	.34		
	30	.53**	.74**	-.74**	.25		
Amino acids	90	.66**	.62**	-.60**			
	70	.55**	.57**	-.54**			
	50	.58**	.63**	-.34			
	30	.23	.20	-.28			
pH	90	-.87**	-.60**				
	70	-.62**	-.92**				
	50	-.70**	-.73**				
	30	-.53**	-.55**				
Free fatty acid	90	.78**					
	70	.96**					
	50	.86**					
	30	.90**					

* Indicates 5% level of statistical significance.

** Indicates 1% level of statistical significance.

Discussion

Many investigators have employed mold, yeast, and bacterial counts to assess the keeping quality of butter. In the present investigation, temperature had a pronounced effect on the association between microorganisms and flavor. Higher correlations were found between flavor score and the numbers of proteolytic, lipolytic, and oxidase producing organisms at 30° and 90° F. than at 50° and 70° F. This finding, and the fact that considerable difficulty is encountered in estimating the true number of organisms present, make it unlikely that any microbiological test employing present methods would prove to be satisfactory for predicting flavor score.

The measurements on the serum fraction were the most promising of the chemical methods investigated for predicting flavor score during storage. In a previous investigation (10) fluorescence measurements of the serum showed possibilities as a test for estimating keeping quality. The present evidence

confirms its usefulness as a guide for investigational purposes, especially under accelerated storage conditions (70° and 90° F.). However, the flavor tests remain the best method of estimating keeping quality.

The free serum acidity, amino acids, and total serum acidity showed no significant differences in regression coefficients between storage temperature, indicating that the rate of formation of acids with flavor score decrease was the same for all the storage temperatures studied. This is one of the essential requirements of an objective test of flavor deterioration. However, the amino acids showed low correlation coefficients at some of the storage temperatures, which prevents their use as a keeping quality test. The remaining two tests were closely associated with flavor deterioration, but no prediction equations were calculated, as it was deemed desirable to base such equations on data from samples obtained from many sources and stored under varying temperatures and humidities. Moreover, because of the complexity of the reactions involved in butter deterioration, it would seem desirable to use more than one test in constructing prediction equations for assessing keeping quality.

Of the objective tests used on the serum fraction the commonly used pH measurement was useful for assessing flavor deterioration in butter stored at low temperatures but not in butter stored at high temperatures. Free serum acidity, total serum acidity, and fluorescence may be applied under accelerated storage conditions to differentiate between butters of good and poor keeping qualities.

As no appreciable oxidative decomposition of the butterfat could be detected by tests of peroxide oxygen or aldehyde content, the free fatty acids of the butterfat were evidently developed by the action of lipolytic enzymes. This lack of appreciable increase in peroxide oxygen and aldehyde content indicates that oxidative changes in the fat fraction contribute little to flavor deterioration in stored salted butter. However, the free fatty acids developed by lipolysis may exert some influence at high storage temperatures.

Decomposition of the serum and flavor deterioration were evident before any free fatty acid or oxidative changes could be detected in the fat. As shown by other workers (4), the antioxidant effects of decomposition products of the serum, e.g., amino acids, may account for the stability of the fat fraction. Flavor deterioration is evidently due to protein decomposition rather than to changes in the fat fraction. The decrease in association between flavor score and amino acids with a decrease in storage temperature indicates that the serum protein was not so completely decomposed at the lower temperatures, that intermediate products are responsible for flavor deterioration, and that deterioration reactions are not the same at all temperatures.

From the results of the chemical and microbiological tests it is apparent that deterioration is retarded in canned butter, especially at the lower temperatures studied. Indeed, canned butter can be stored at 30° F. for periods up to 45 weeks without appreciable lowering of its quality. Therefore canned butter can be stored and transported at chill temperatures rather than at the freezing temperatures required for butter in prints.

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APPENDIX TABLE I

FLAVOR PANEL SCORES AND OFFICIAL GRADERS' SCORES OF BUTTER FROM PLANT A

Storage temperature, °F.	Storage time, days	Canned		Print	
		Panel	Graders	Panel	Graders
30	Initial	7.2	39.0	7.5	38.5
	16	7.7	40.0	7.2	39.5
	32	7.5	38.5	5.9	38.0
	64	6.1	38.0	3.7	39.0
	128	7.4	39.0+	4.3	39.5
	192	6.6	39.0	4.1	—
	256	7.6	38.0	4.0	36.0—
	321	6.5	39.0	2.8	37.0
	385	6.9	—	0.0	—
	Initial	7.2	39.0+	7.5	38.5
	4	7.3	39.0	7.4	39.0
	8	7.0	39.0	6.9	38.5
	16	7.1	39.0—	6.8	39.5
	32	6.5	36.5	5.6	38.5
50	64	3.3	37.0	0.9	36.0
	96	4.9	36.0	2.4	36.0
	128	4.9	—	0.7	—
	192	6.1	37.5	2.0	—
	256	5.9	38.0	0.0	—
	Initial	7.2	39.0+	7.5	38.5
	0.5	7.3	38.5	7.4	38.5+
	1	7.0	39.0—	6.9	39.0
	2	7.3	39.0—	7.2	38.5
	3	7.0	39.0	6.7	39.0—
70	4	6.8	39.0	6.9	39.0—
	8	6.5	37.5	6.2	39.0+
	16	6.1	38.5	6.1	37.5
	32	5.1	37.0	4.4	36.5
	64	3.2	38.0	1.2	35.0
	128	4.2	—	1.6	—
	Initial	7.2	39.0+	7.5	38.5
	0.25	7.4	39.0+	7.5	39.5
	0.5	—	37.0	—	38.5
	1	6.7	38.5	6.5	39.0
90	2	6.0	39.0—	6.2	38.5
	3	6.3	39.0	6.4	39.0—
	4	6.3	39.0—	6.2	38.5
	8	5.3	38.0—	5.2	38.0+
	16	4.6	37.5+	5.0	38.5—
	32	3.6	39.0—	4.7	39.0

APPENDIX TABLE II

FLAVOR PANEL SCORES AND OFFICIAL GRADERS' SCORES OF BUTTER FROM PLANT B

Storage temperature, °F.	Storage time, days	Canned		Print	
		Panel	Graders	Panel	Graders
30	Initial	8.9	39.0—	8.7	39.0
	16	7.4	39.5+	6.9	39.0—
	32	7.2	39.5	6.9	39.0+
	64	7.5	39.0	6.4	36.0
	128	7.6	39.0—	4.2	38.0
	192	7.4	37.0	2.6	—
	256	6.3	37.0	3.8	—
	321	6.9	39.0—	3.4	36.0
	385	4.8	—	0.0	—
50	Initial	8.9	39.0—	8.7	39.0
	4	6.9	39.0	7.2	39.0
	8	7.1	39.0	7.4	38.5
	16	7.4	39.5—	5.9	39.0+
	32	5.1	38.0	4.5	37.0
	64	6.6	39.0	2.3	36.5
	96	4.6	38.0	1.5	36.0
	128	6.3	39.0	1.5	36.0
	192	6.5	38.0	1.2	—
	256	5.5	37.0	0.0	—
70	Initial	8.9	39.0—	8.7	39.0
	0.5	7.8	38.5	7.8	39.0
	1	7.7	39.5	7.7	39.0
	2	7.1	39.5	7.7	39.0
	3	7.5	39.5—	6.4	39.0
	4	6.9	39.0	6.9	39.0—
	8	6.1	37.5	7.2	37.5
	16	6.7	39.0	5.1	38.0—
	32	4.4	35.0	2.8	36.0
	64	2.5	35.5	1.0	36.0
90	128	3.3	—	2.6	—
	Initial	8.9	39.0—	8.7	39.0
	0.25	7.3	38.5	7.2	39.0—
	0.5	7.0	38.0	7.2	38.0
	1	6.5	38.5	6.9	38.0
	2	6.5	38.0	6.1	38.0
	3	6.0	38.0+	4.8	38.0—
	4	6.0	39.0—	5.2	38.0
	8	6.5	37.5	4.1	37.0
	16	5.3	38.5	3.8	37.0—
	32	5.2	39.5+	4.2	39.5—

THE OXIDATION, IGNITION AND DETONATION OF FUEL VAPORS AND GASES

III. THE CAUSE OF THE EFFECT OF METALLIC DOPE TO DELAY DETONATION¹

By R. O. KING²

Abstract

The antiknock effect of metallic dope is attributed to the catalytic action of the surface, maintained in an oxidizing atmosphere by continuous deposition thereon of the metal of the dope, to oxidize the fuel in part to steam and carbon dioxide, the consequent dilution of the end gas causing a reduction of inflammability sufficient to prevent completion of combustion in other than the normal manner. Experiments indicate that temperatures required for the necessary catalytic activity are attained during the period of flame travel; not prior to ignition. In support of the theory experimental evidence is given showing that, (a) steam is especially effective to reduce inflammability, (b) doped pentane or hexane oxidizes without ignition to steam and carbon dioxide only in reaction chamber No. 10, described in Part I, at any temperature of reaction, (c) the carbon dioxide-steam reaction is inhibited by a sulphur catalyst poison and the similar action in the engine destroys the antiknock effect of the dope. It is shown further by experiments with and without additions of a catalyst poison to *undoped* engine fuel that, in conditions leading to high surface temperatures in the combustion space, a carbon dioxide-steam reaction having a considerable antiknock effect is obtained. The engine experiments with catalyst poisons are completed by obtaining conditions in which tetraethyl lead becomes a pro-knock. It is recognized that the catalyst theory depends fundamentally on the oxidation of hydrocarbon fuel being a heterogeneous reaction as indicated by the experiments described in Part II, and some further evidence in support of the view, obtained by using catalyst poisons, is given in this Part.

Introduction

The discovery by Midgley and Boyd of the remarkable effect of tetraethyl lead present in extremely small concentration in engine fuel, to delay the onset of detonation as the compression ratio is raised, was followed by a spate of explanatory theories, the number extending ultimately to more than a dozen. Those proposed prior to 1926 and reviewed by Clark and Thee (5) did not involve a departure from accepted belief concerning the mechanism of the oxidation of the paraffin hydrocarbons present in large proportion in normal engine fuel and mainly responsible for the occurrence of detonation.

Such a departure was made in the Callendar nuclear drop-peroxide theory (3, 4) submitted to the Aeronautical Research Committee, December, 1926, in that oxidation was taken to begin with the formation of an organic peroxide instead of an hydroxyl compound as required by the generally accepted, Armstrong-Bone hydroxalation theory. Support was afforded the peroxide theory by the work of Moureu, Dufraisse, and Chaux who followed Callendar in associating peroxides with fuel detonation (15).

¹ Manuscript received in original form August 11, 1947, and, as revised, November 25, 1947. Contribution by Defence Research Board (Canada).

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Egerton and Gates (6), in a review of the theories of antiknock action, agreed that peroxides, acting as autocatalysts, are formed in the early stage of combustion and suggested that metallic antiknocks form comparatively stable peroxides which react with and destroy the fuel peroxides which are then regenerated. The suggestion led Egerton (7, pp. 2911-2926) to the formulation of a chain reaction theory in which peroxide is an essential link, the development of the reaction to cause knocking being interrupted on the destruction of the peroxide by the metal of the dope, which is oxidized in the process. Finally, Beatty and Edgar (2, pp. 2927-2936) in a comprehensive review of the theory of knock in internal combustion engines conclude that "antiknock agents act as inhibitors for the slow oxidation reactions in the end gas. Their effect is to break short the reaction chains and so prevent the chain development from reaching that critical point at which its multiplication begins".

Theories that antiknocks act by destroying organic peroxides or by breaking reaction chains in an homogeneous fuel-air mixture are not accepted but discussion can be reserved. The reviews mentioned do, however, deal with two matters related to experimental work described in Parts I (8) and II (9) and later in this Part.

Beatty and Edgar mention particularly the difficulty of relating oxidation as it occurs in laboratory experiments to the similar effect in the end gas of an engine. Thus it is stated that laboratory oxidations cannot be carried to temperatures higher than 500° C. because of the incidence of ignition or explosion, and that time of reaction is sometimes 1000-fold greater than in an engine. The statements were, of course, made before the development of reaction chamber No. 10, described in Part I (8) in which it is possible to carry laboratory oxidations of hydrocarbons commonly used as engine fuel to whatever temperature is required for completion, 700° C. or over, without ignition and in reaction times of a second or less.

The positive catalyst theory, which assumes that antiknocks accelerate oxidation *prior to ignition* in the engine and accordingly weaken the mixture to an extent sufficient to prevent detonation, is mentioned by Egerton with the comment that the antiknocks retard oxidation and consequently the theory is contrary to fact. Beatty and Edgar also mention the theory and dismiss it on sounder grounds by observing, in effect, that promotion of the oxidation of the fuel by antiknocks during the *early stages of combustion* in an engine is not in accordance with experimental facts.

Revised Positive Catalyst Theory

The experiments described in Part I (8) and others to be described in this Part show that the oxidation of paraffin hydrocarbons doped with iron carbonyl, in reaction chamber No. 10, which provides conditions approaching those obtaining in the combustion space of an engine, is a heterogeneous reaction on a surface of iron maintained as such in an oxidizing atmosphere by continuous deposition of metal from the organic compound. The final

products only, namely steam and carbon dioxide, are produced at any temperature of reaction. The reaction does not proceed with high velocity until surface temperature exceeds 500°C . Such high surface temperatures would be found in the combustion space of an engine on the exhaust valves in conditions of maximum power output and momentarily on other surface exposed to radiation from the advancing flame which reaches temperatures of 2500°C . and over, depending on compression ratio and other factors. The end gas in which detonation occurs is heated by compression to temperatures of 650°C . and over, depending on compression ratio, and would be expected to attain even higher temperatures because of turbulence. Temperature and turbulence conditions are, therefore, as required to promote extremely rapid surface oxidation of the doped fuel to final products which could reduce the inflammability of the end gas to such an extent that completion of combustion would be possible solely by normal flame travel. An adequate explanation for the antiknock action of metallic dopes is then obtained without having to determine the cause of detonation.

Section I

EFFECT OF STEAM TO REDUCE INFLAMMABILITY

The effect of steam, nitrogen, and carbon dioxide as diluents on the inflammability of a normal fuel-air mixture used in the E 35 engine was determined by Ricardo (17). The work was extended and the experimental results discussed some time later by Alcock (1). The gases mentioned were added to the fuel-air charge in increasing proportion until inflammability was so reduced that misfiring occurred. It was emphasized that elaborate precautions, including superheating, were required to ensure that steam was added to the engine charge as such, not as part water.

It was found that 8.9% of steam sufficed to reduce inflammability to the extent required to cause misfiring although flame temperature was reduced by 125°C . only. Carbon dioxide was required in the proportion of 19.6% to produce a similar effect although flame temperature was reduced by 400°C . The conclusion was that steam exerted a nonthermal effect to reduce inflammability, the nature being unknown. Whatever the nature of the effect may be, the magnitude is of great importance, and from the data given above it is calculated that, on a weight basis, steam is six times more effective than carbon dioxide, the other product of the complete combustion of hydrocarbons.

Effect of Steam to Reduce the Inflammability of Hydrogen

Hydrogen is especially suitable for experiments to determine the effect on inflammability of steam which is the sole final product of oxidation. It was mentioned, Part I (8), that tetraethyl lead and iron carbonyl had been shown by Mardles to promote the oxidation of hydrogen. The rate of oxidation was not, however, related to inflammability, and the experiment using the carbonyl as the oxidant has been repeated in carefully controlled

conditions and using a conventional flow method. The combustion tube was of silica, 1 in. internal diameter, supported in a vertical 6 in. furnace. Silica was selected because of its relatively inactive surface. The hydrogen and air were from high pressure cylinders and, therefore, nearly dry, but, as a further precaution, the gases were passed over phosphorus pentoxide while en route to the combustion tube. The reacting mixture was supplied at the rate of 200 cc. per min. and contained hydrogen in the concentration of 40% by volume. Iron carbonyl, as vapor, was added to the air stream at the rate of 40 mgm. per hour. Temperatures were taken by means of a thermocouple in a silica sheath placed at the position of maximum temperature on the longitudinal axis of the combustion tube. The hot gases from the combustion tube were passed through a Liebig condenser and then through a U-tube

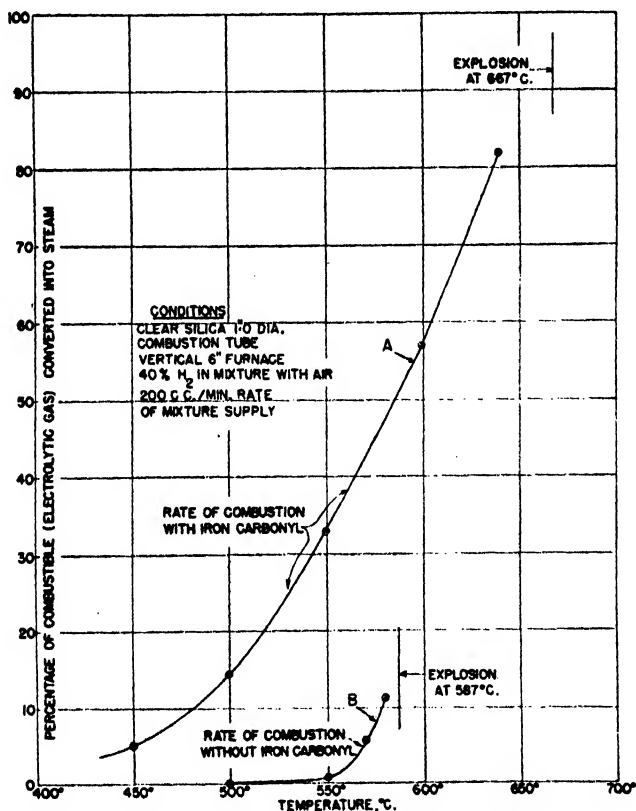


FIG. 1. Graphs showing the effect of steam from a heterogeneous reaction to reduce inflammability and thereby raise explosion temperature.

containing calcium chloride. Rates of oxidation were measured by weighing the water of combustion at suitable time intervals. When iron carbonyl was added to the reacting mixture, iron oxide was deposited on the tube at the positions of the upper and lower convection circulation, see Fig. 5, Part I (8), and in view of the fact that the mixture contained both oxidizing and reducing

gases, care was taken that the equilibrium oxide had formed prior to measuring rate of combustion. Equilibrium was taken as having been established at a particular temperature when water of combustion was obtained at a constant rate.

Graph *A* of Fig. 1 gives rates of steam formation when the hydrogen-air mixture contained the vapor of iron carbonyl, and Graph *B*, rates of steam formation when the mixture without the vapor was passed through the tube in clean condition. It will be noted that with iron carbonyl present combustion of electrolytic gas occurred at the easily measurable rate of 5%, at 450° C., whereas the rate was about 1% only at 550° C., in the absence of the carbonyl and 33-fold greater when it was present. The mixture containing iron carbonyl exploded at 667° C. and at 587° C., in the absence of the carbonyl.

Concluding Comments

The experiments by Ricardo and Alcock show the effect of steam from an outside source to reduce the inflammability of the reacting mixture in an engine. Those just described show a similar effect obtained by steam produced by the reaction itself.

Section II

THE OXIDATION OF PENTANE IN REACTION CHAMBER NO. 10, AS AFFECTED BY IRON CARBONYL

The reaction chamber was described in Part I (8), and experiments on the effect of flow configuration described in Part II (9) indicated that oxidation in the chamber is a heterogeneous reaction so far as doped pentane is concerned and probably of a similar character in respect of pentane alone. Experiments described in this section were made to confirm the earlier results and to determine the effect on rate of oxidation of changing the concentration of iron carbonyl and the effect of a residual surface of iron oxide.

The experimental results shown by the graphs of Figs. 7, 8, 9 and 10 of Part I (8) were obtained immediately after the completion of the reaction chamber. The chamber was then dismantled, cleaned with hydrofluoric acid, washed with steam, and an oxidation of pentane containing iron carbonyl in the concentration of 0.5% repeated. The experimental results are plotted on Graph *B* of Fig. 2, together with those obtained earlier, and it will be noted that the two sets of results fall on a single curve showing a degree of repeatability not generally obtained when using conventional methods.

The increase in rate of reaction obtained on doubling the dope concentration is shown by Graphs *B* and *C* of Fig. 2. A useful comparison can be made at the temperature of 550° C., when about half of the oxygen remained uncombined. The increase was from 4.1 to 5.5 moles of oxygen reacted, that is, 30%. Flow configuration was similar for both experiments and the increase is attributed to some possible increase in the area of the effective catalytic iron surface or to an increase in the density of the catalyst.

Rates of formation of carbon oxides for the smaller concentration of iron carbonyl were given by the graphs of Fig. 8, Part I (8). Exactly similar results were obtained when using the larger concentration and as before reaction was substantially to steam and carbon dioxide whatever the temperature.

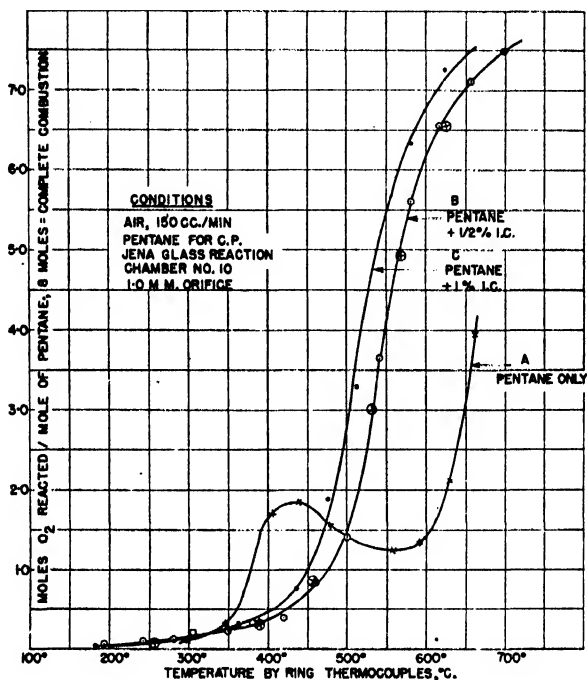


FIG. 2. Graphs showing the increase in velocity of the carbon dioxide-steam reaction due to doubling the iron carbonyl concentration in pentane.

Pentane Oxidation on Residual Oxide Surface

The coating of the surface of the reaction chamber with iron and iron oxides seen after oxidation of pentane doped with iron carbonyl was shown, *B*, Fig. 6 of Part I (8); distribution varies with rate of mixture supply and the concentration of iron carbonyl in the pentane and thickness with time of use of the doped pentane, but the surface becomes completely coated with brick red oxide on continued use of the chamber with undoped mixture. The results of an oxidation of pentane after use of the chamber with pentane containing iron carbonyl in the concentration of 1.0% are given by Graph *C* of Fig. 3. Graph *A* for pentane oxidized in the chamber when clean and Graph *B* for the oxidation of pentane plus 1.0% iron carbonyl are given for case of comparison. The graphs show that when the metal surface was no longer maintained by continuous deposition from the carbonyl, rates of reaction at temperatures above 500°C. are greatly reduced and tend to approach those obtained when the reaction chamber surface is clean glass. Thus at 550°C. rate of reaction fell from 5.2 moles, Graph *B*, to 1.8 moles of oxygen reacted, Graph *C*. At 625°C., oxygen was reacted at the rate of

7.25 moles when using the doped mixture, Graph B, but diminished to 5.8 moles for the residual surface, Graph C, and further to 4.6 moles after $3\frac{1}{2}$ hr., as shown by the single observation marked with an arrow below Graph C of the figure.

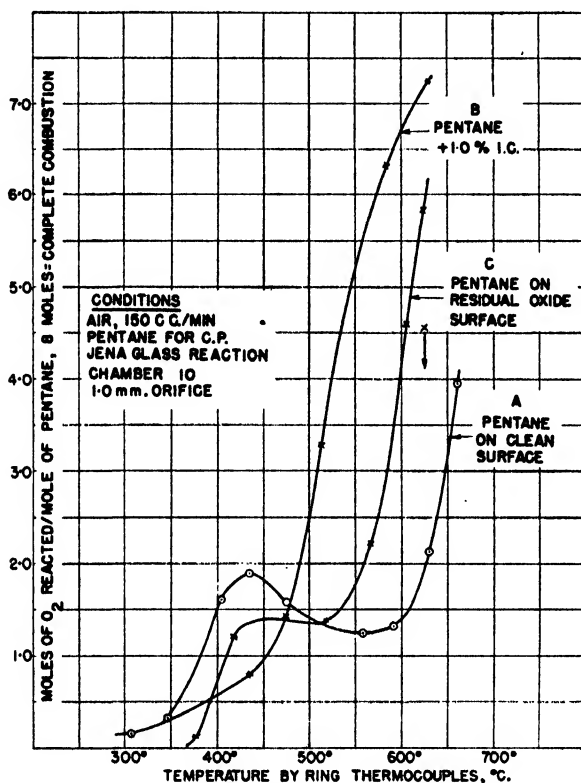


FIG. 3. Graphs showing the effects on the oxidation of pentane of ceasing to maintain the catalytic surface provided by continuous deposition of iron from the carbonyl.

The reappearance of the aldehyde hump, Graph C of Fig. 3 when the active metal surface of the reaction chamber surface was converted to oxide is of great interest and supports the view, expressed in Section V of Part II (9), that the oxidation of pentane to partial products, including aldehyde, is a heterogeneous reaction.

Section III

THE OXIDATION OF HEXANE IN REACTION CHAMBER NO. 10, AS AFFECTED BY IRON CARBONYL

Hexane is present in considerable proportion in normal engine fuel and is of relatively low octane number. Experimental results for the effect of metallic antiknocks on the oxidation of the substance, hitherto published, have always been obtained by conventional methods and because of the almost complete oxidizing nature of combustible mixtures with air, reaction could not occur on a surface of metal deposited from the dope, except at very

low temperatures. The consequent effect of the dope to inhibit the oxidation of hexane and higher paraffins in the same circumstances is the experimental basis of current theory attributing the antiknock action to an antioxidant property. It became of special interest, therefore, to determine if the oxidation of hexane in reaction chamber No. 10 at high temperatures would be promoted on the addition of metallic dope and if reaction would be to final products as for pentane oxidation.

Oxidations in Reaction Chamber No. 10

The experimental conditions were as described for oxidations of pentane. The 'hexane', supplied by the Anglo-American Oil Company, was procured from the fractional distillation of nearly aromatic-free petroleum spirit. The density was 0.6965, and distillation range 62° to 85° C. for a 95% fraction.

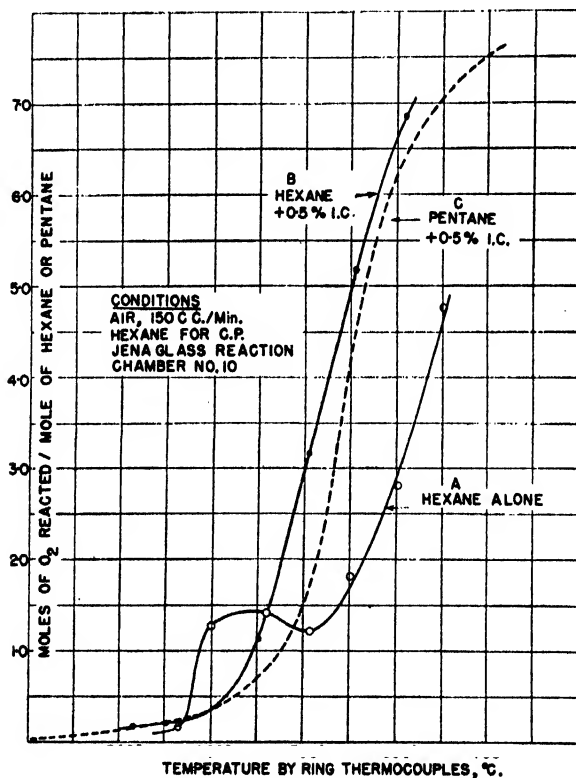


FIG. 4. Graphs showing the effect of iron carbonyl to promote the oxidation of hexane at high temperatures as compared with the similar effect for pentane.

Experimental results are given by the graphs of Fig. 4: Graph A is for hexane alone in the reaction chamber in clean condition; Graph B is for hexane plus iron carbonyl in the concentration of 0.5%. The combining proportions mixtures used for the experiments were made up on the assumption that the hexane was normal and that $9\frac{1}{2}$ moles of oxygen would be required accordingly

for the complete oxidation of one mole of the paraffin. It will be noted that the characteristics of hexane oxidation are similar to those determined for the oxidation of pentane. Graph C of the figure, for the oxidation of doped pentane, is reproduced from Fig. 2 and appears to show that iron carbonyl possesses the greater oxidation promoting effect in respect of pentane, but, when allowance is made for the specific oxygen consumption, the carbonyl is found to be of equal effect in respect of the two paraffins, as nearly as can be determined without exact knowledge of molecular composition.

The oxidation of doped hexane was, as for doped pentane, substantially to steam and carbon dioxide at any temperature of reaction, as shown by the graphs of Fig. 5.

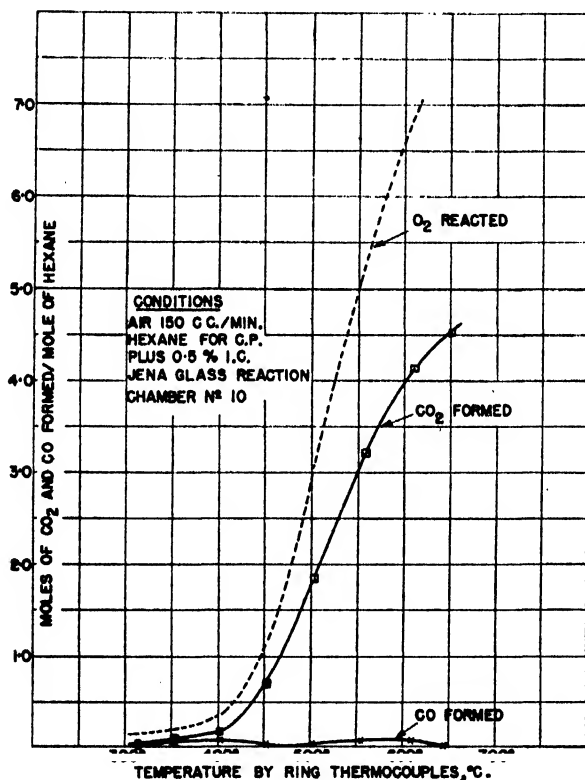


FIG. 5. Graphs showing that the oxidation of hexane containing iron carbonyl is substantially to carbon dioxide and steam at all temperatures of reaction.

Section IV

THE SPECIFIC EFFECT OF ETHYL MERCAPTAN TO INHIBIT THE HETEROGENEOUS REACTION OF PENTANE AND HEXANE TO STEAM AND CARBON DIOXIDE

Having shown that the antiknock, iron carbonyl, suppresses the formation of partial oxidation products, including aldehyde, and promotes the formation of steam and carbon dioxide at all temperatures of reaction, it remains to

determine which of the two effects is responsible for the antiknock property of the carbonyl. The use of a catalyst poison in oxidation and related engine experiments makes it possible to distinguish between the effects mentioned.

Ethyl Mercaptan and Hydrogen Sulphide

The one hydrogen atom of the mercaptan and the two of the sulphide are replaceable by metal. Either substance converts a contact surface of iron to one of iron sulphide and is without effect on a surface of iron oxide. Both substances were known from earlier experiments to destroy the antiknock effect of the metallic dopes. The mercaptan, rather than hydrogen sulphide, was used for laboratory experiments to avoid the complications involved in the supply and measurement of the sulphide at the small rates required. The concentration of 2.5% by weight of the mercaptan in the pentane and hexane is without significance except that in engine experiments it was sufficient to destroy the antiknock effect of 2 cc. per gal.* of tetraethyl lead in an engine fuel.

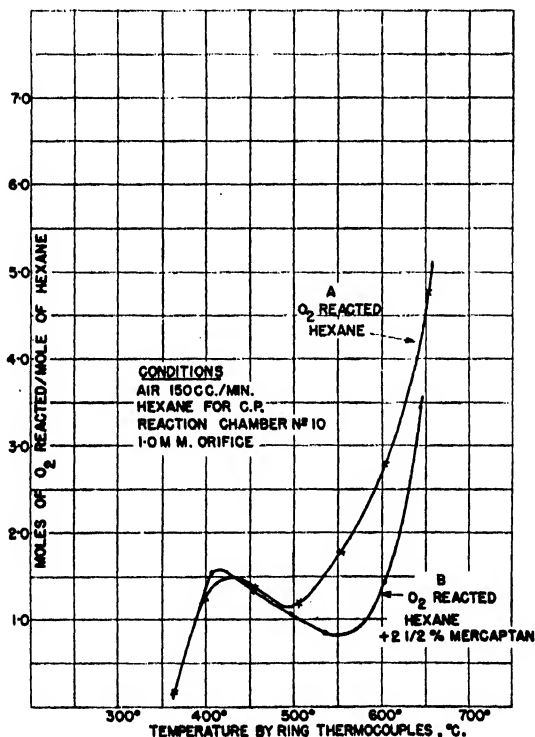


FIG. 6. Graphs showing that ethyl mercaptan, a catalyst poison, does not affect the aldehyde reaction in a glass reaction chamber (No. 10).

Effect of Ethyl Mercaptan on the Oxidation of Hexane in Reaction Chamber No. 10

The experimental results are given by the graphs of Figs. 6, 7, and 8. It is of special significance, as shown by the graphs of Fig. 6 for oxygen reacted,

* References throughout this paper are to the imperial gallon.

that the mercaptan had no measurable effect on reaction velocities at temperatures below about 480°C. , that is, at the temperatures of the formation of partial products including aldehyde. The inhibitory effect was confined to the carbon dioxide-steam reaction as shown by the graphs of Figs. 7 and 8 for rates of formation of carbon oxides.

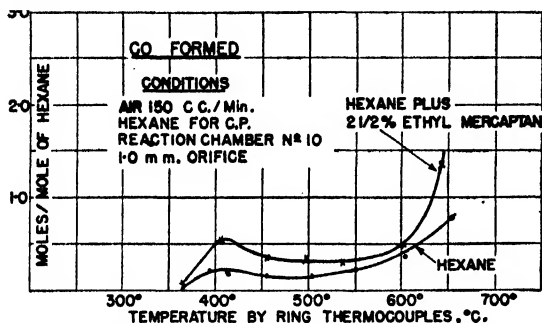


FIG. 7. Graphs showing the effect of ethyl mercaptan on carbon monoxide formation when hexane is oxidized in reaction chamber No. 10.

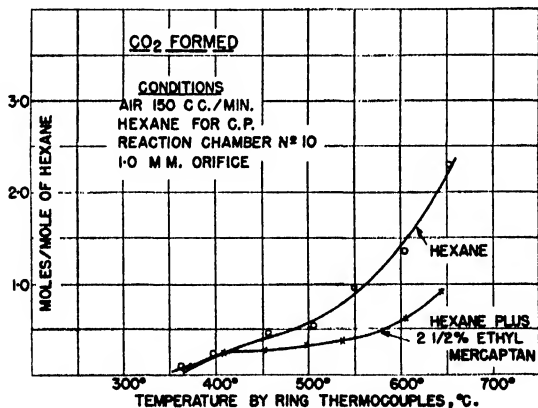


FIG. 8. Graphs showing the effect of ethyl mercaptan on carbon dioxide formation when hexane is oxidized in reaction chamber No. 10.

Effect of Ethyl Mercaptan on the Oxidation of Hexane plus Iron Carbonyl in Reaction Chamber No. 10

The experimental results are given by the graphs of Figs. 9, 10, and 11. At 550°C. oxygen was reacted at the rate of 5.0 moles when the pentane contained 0.5% of iron carbonyl, Graph A, Fig. 9. The rate was 1.2 moles only when the doped pentane contained $2\frac{1}{2}\%$ of mercaptan. Carbon dioxide, at the same temperature, was formed at the rate of 1.75 moles without the mercaptan and 0.25 moles with it. Carbon monoxide formation, Fig. 11, was inappreciable in either case. At 600°C. oxygen reacted was 6.6 moles without the mercaptan and 0.8 moles with it. There was a corresponding change in rate of carbon dioxide formation, and carbon monoxide formation occurred at an appreciable rate, 0.25 moles.

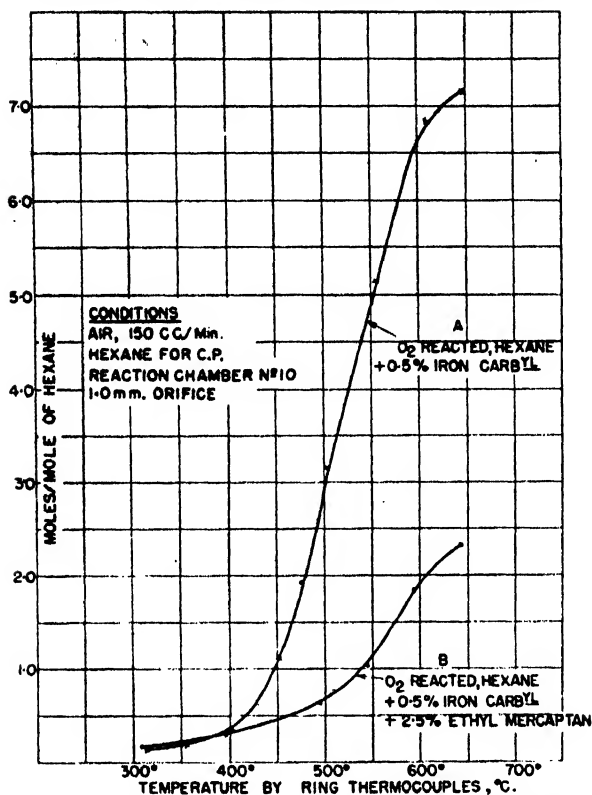


FIG. 9. Graphs showing the inhibiting effect of ethyl mercaptan on the oxidation of hexane doped with iron carbonyl in glass reaction chamber (No. 10).

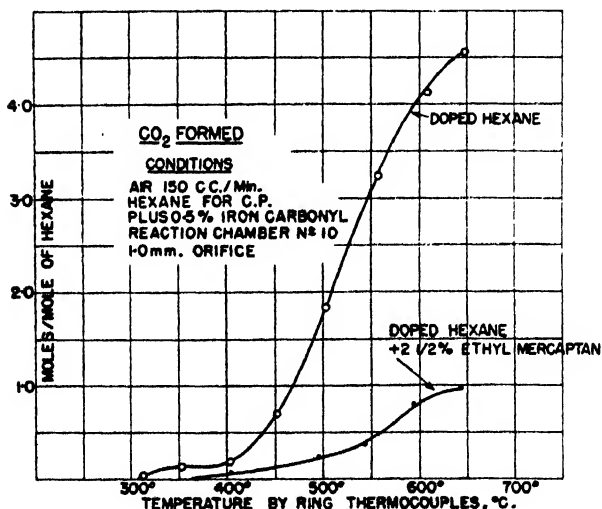


FIG. 10. Graphs showing the effect of ethyl mercaptan on carbon dioxide formation when doped hexane is oxidized in glass reaction chamber (No. 10).

The Effect of Ethyl Mercaptan on the Oxidation of Pentane in Reaction Chamber B, Fig. 11, Part II (9)

The reaction chamber was of mild steel which does not rust uniformly. The surface in contact with the reacting mixture of pentane-air would, therefore, comprise areas of iron oxide which would promote the formation of

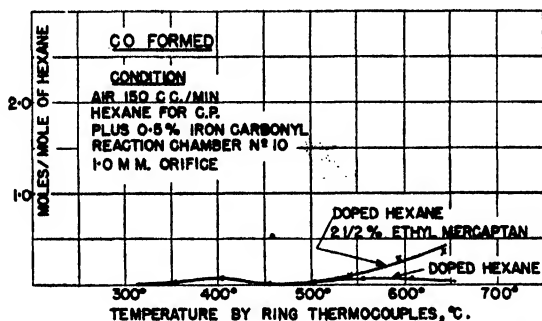


FIG. 11. Graphs showing the effect of ethyl mercaptan on carbon monoxide formation when doped hexane is oxidized in glass reaction chamber (No. 10).

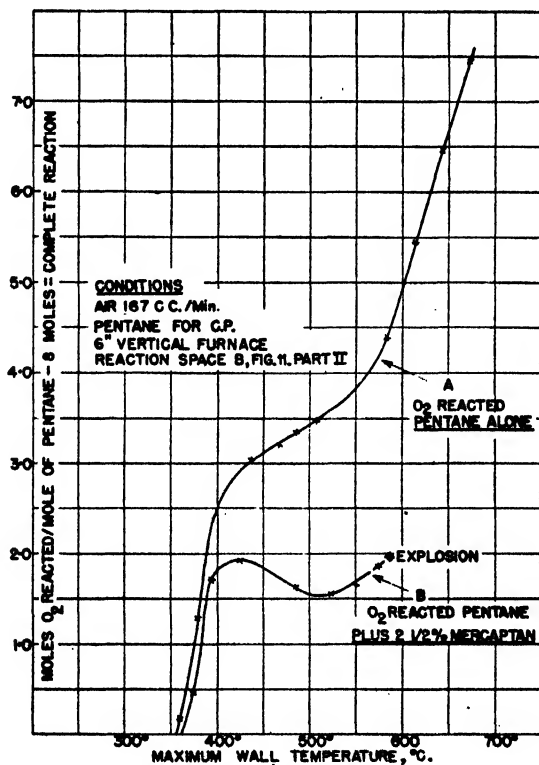


FIG. 12. Graphs showing the effect of ethyl mercaptan on the oxidation of pentane (undoped) in a steel reaction chamber.

partial oxidation products and areas of iron which would promote oxidation to final products, and, as there existed a steep temperature gradient over the length of the chamber, reaction can occur at a range of temperatures even when the maximum is 600°C. or over. The mixed nature of the reaction in the chamber is shown by Graph A of Fig. 12, which is characteristic of both the aldehyde and the carbon dioxide-steam reactions. The effect of the mercaptan is shown by Graph B of the figure. The carbon dioxide-steam reaction is nearly eliminated, as shown by the graphs of Figs. 13 and 14, leaving the aldehyde, which, in the absence of dilution with steam and carbon dioxide, ignites and explodes when the temperature reaches 590°C.

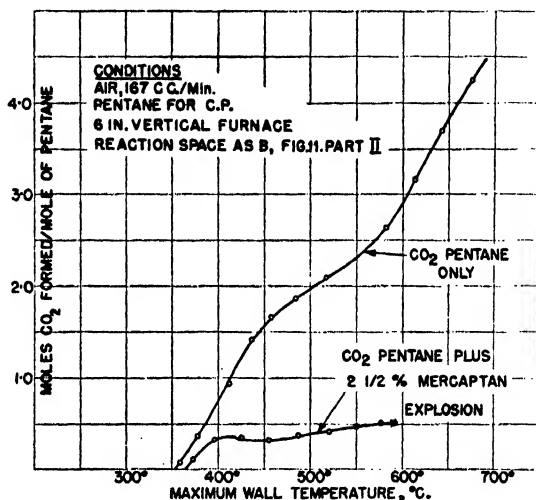


FIG. 13. Graphs showing the effect of ethyl mercaptan on carbon dioxide formation when pentane is oxidized in the steel reaction chamber.

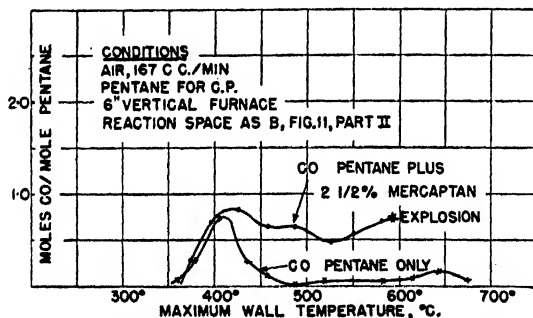


FIG. 14. Graphs showing the effect of ethyl mercaptan on carbon monoxide formation when pentane is oxidized in the steel reaction chamber.

Pentane Oxidation on Surface Remaining after the use of Mercaptan

An oxidation of pentane in the steel reaction space, as above, was carried out after the oxidation of pentane plus the mercaptan. The experimental

results are given by the graphs of Fig. 15 and show a considerable residual effect. Thus, for example, at 550° C., 3.8 moles of oxygen were reacted when the reaction chamber was first used. The rate dropped to 1.7 moles (Fig. 12) when the mercaptan was present and rose to 2.3 moles only on the residual surface (Fig. 15). The rates of carbon monoxide and carbon dioxide formation

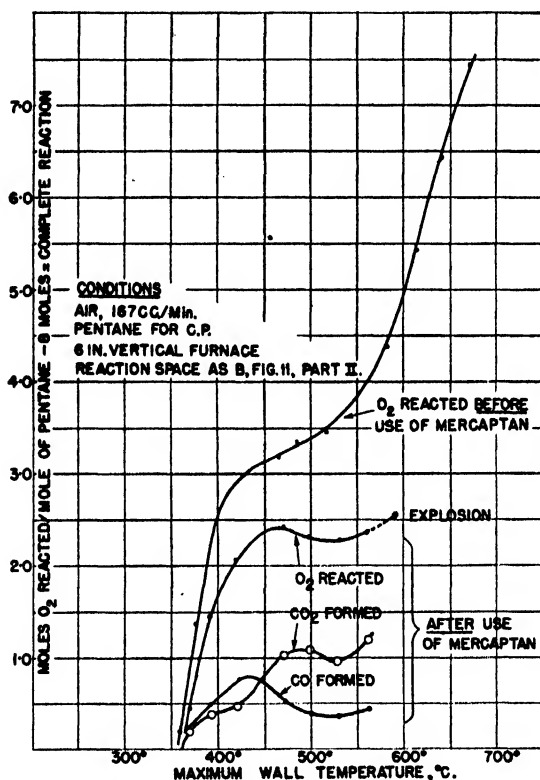


FIG. 15. Graphs showing the effect of the surface of iron sulphide remaining after the use of ethyl mercaptan on the oxidation of pentane in the steel reaction chamber.

on the residual surface are given by the lower graphs of Fig. 15 and comparing them with the graphs of Figs. 13 and 14 for pentane plus the mercaptan it will be seen that change of rates of carbon dioxide and carbon monoxide formation is in accordance with the changes in rates of oxygen reacted.

Conclusions

The experiments described in this section help to confirm that the oxidation of pentane is a heterogeneous reaction and show definitely that it is possible by the use of a catalyst poison to determine whether the antiknock action of metallic dope is due to the effect to inhibit the aldehyde reaction or the effect to promote reaction to final products.

Section V

THE PRO-KNOCK EFFECTS OF LUBRICATING OILS, ETHYL MERCAPTAN, AND HYDROGEN SULPHIDE

An extensive series of experiments, made some years ago by King and Moss (10, 11, 13, 14) demonstrated that lubricating oils when added to engine fuel varied in pro-knock effect. The greatest effect was obtained when the oils were added to doped fuels. Olein or oleic acid in a concentration of 1.0% only in the fuel destroyed almost the entire antiknock effect of nickel carbonyl in the large concentration of 10 cc. per gal. in the fuel, and was of similar effect in respect of iron carbonyl, but a concentration of 12% of olein in the fuel was required to destroy 85% of the antiknock effect of a 12 cc. per gal. addition to the fuel of tetraethyl lead. Castor oil, which is soluble in engine fuel to the extent of about 1½% only, was as effective as olein in destroying the antiknock value of nickel carbonyl, somewhat less effective in respect of iron carbonyl but was found to be of no *antiknock* effect when added to fuel doped with tetraethyl lead. The effect of the rape oils which are soluble in any concentration was similar to that of castor. The mineral oils were quite effective in reducing the antiknock value of the carbonyls but large additions were required in respect of tetraethyl lead even to obtain a relatively small effect.

The variation of the pro-knock effect with the natures of the oils and the metals of the dopes could not be explained in terms of theories based on homogeneous reactions, and little information was available about the effect of the several oils on heterogeneous reactions when the contact surfaces were of iron, nickel, or lead. It was known, however, that olein or oleic acid is a poison in respect of nickel catalysts (18, p. 909). Comment was made accordingly in the published account of the experiments and no further explanation attempted.

Similar engine experiments were made later using ethyl mercaptan and hydrogen sulphide additions to engine fuel instead of lubricating oils. The substances, added in small proportion, destroyed completely the antiknock effects of tetraethyl lead and iron carbonyl and gave rise to further pro-knock effects which will be described later. Again the experimental results could not be explained by accepted theory. The sulphur compounds were known catalyst poisons in respect of the carbon dioxide-steam reaction on iron and nickel surfaces, but an explanation of their pro-knock effect given accordingly would have involved the assumptions that catalytic surfaces were provided in the combustion space by the metallic dopes and that the steam formed on them in the absence of a catalytic poison was responsible for the antiknock effect. The experimental results were, therefore, withheld from publication until experiments could be made on the oxidation of hydrocarbon engine fuel at the high temperature of the 'end gas' and on the effect of sulphur catalyst poisons on the reactions.

Selection of Sulphur Catalyst Poison

It was a convenience to use a liquid compound soluble in engine fuel, and thiophene, carbon disulphide, and ethyl mercaptan were tried. The pro-knock effects of the compounds on straight run aviation petrol doped with 2.0 cc. per gal. of tetraethyl lead when used in the C.F.R. engine with unheated induction, are shown by the graphs of Fig. 16. It will be seen that all three

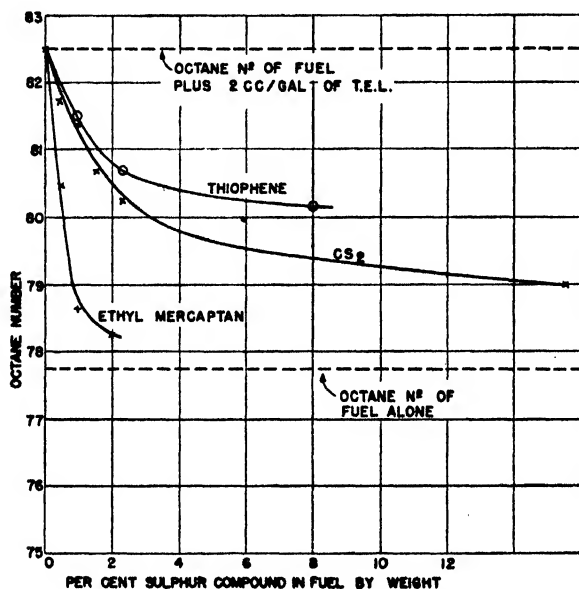


FIG. 16. Graphs showing the pro-knock effect of three sulphur compounds when added to a low octane number engine fuel doped with tetraethyl lead. C.F.R. engine.

substances were pro-knockers and that the mercaptan was outstanding, a concentration of 2% in the fuel being sufficient to destroy nearly all of the effect of tetraethyl lead to raise the octane number of the fuel from 77.8 to 82.5. It was not possible to prevent the loathsome odor of the mercaptan from reaching many parts of the building in which the engine was situated, and hydrogen sulphide was used as an equivalent catalyst poison for further experiments.

Engine Experimental Conditions

The experiments were made with a variety of hydrocarbon fuels used in the C.F.R. research engine. The intake air was unheated in some cases and in others raised to 300° F. as required for the standard method of determining octane number. The knocking tendency of the fuels was generally obtained by the H.U.C.R. method as used in the Air Ministry Laboratory (12), but sometimes by determining octane number. Some experiments were, however, made with very weak or very rich mixtures. Tetraethyl lead was used as the fuel dope in preference to iron carbonyl which on long continued use, especially in large concentration, destroys spark plug insulation and leaves

heavy deposits of oxide in the engine combustion space. The engine experimental results are given by a series of graphs and the experiments are described in succeeding paragraphs.

Hexane Experiments

Experiments with hexane as an engine fuel are of special interest because of the oxidation experiments described in Sections III and IV. The experiments were made with increasing additions of hydrogen sulphide when using either hexane alone or hexane plus 8.0 cc. of tetraethyl lead per gallon and when using correct, rich, and weak mixtures and heated and unheated air supply.

The experimental results are shown by a series of graphs, Fig. 17, H.U.C.R. being plotted against hydrogen sulphide additions. Mixture strengths are

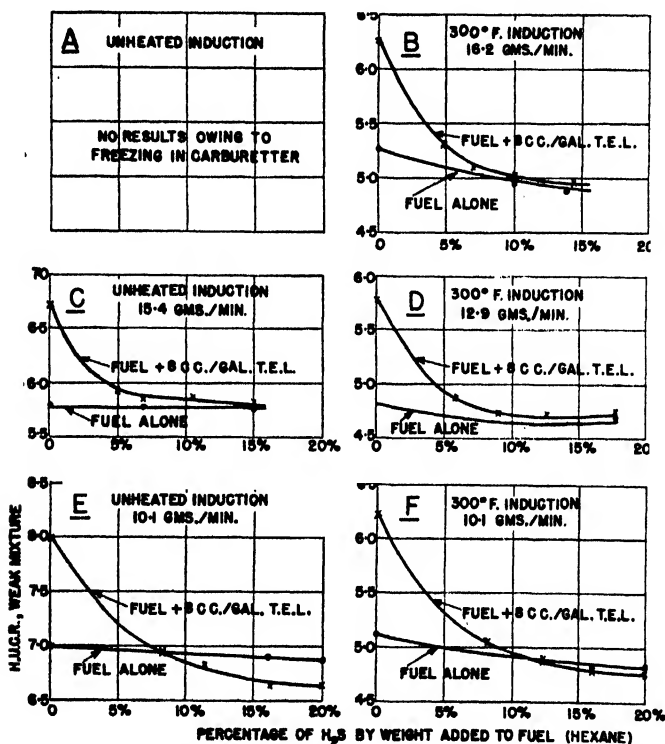


FIG. 17. Graphs showing the pro-knock effect of hydrogen sulphide in respect of hexane doped with tetraethyl lead. C.F.R. engine, for correct, rich, and weak mixtures and heated (300° F.) and unheated induction.

shown by the figures for fuel consumption in grams per minute. Considering first the results for correct mixture strength, Graphs C and D, it will be seen that with unheated induction, Graph C, H.U.C.R. increased from 5.75 to 6.7 on adding the dope to the pentane and then diminished to 5.9 when hydrogen sulphide was added in the concentration of 5%, that is, 85% of the antiknock

value of the dope addition was destroyed. On increasing the hydrogen sulphide addition even to the large concentration of 15% of the weight of the fuel, nothing more happened than the complete destruction of the antiknock effect of the metallic dope.

The engine would not run on hexane at high compression ratios without excessive detonation unless the mixture were very weak or very rich, and results of experiments made accordingly and with heated or unheated induction are given by the Graphs *B*, *E*, and *F* of Fig. 17. The graphs show that by using the hexane at a relatively high compression ratio or with a high induction temperature a small pro-knock effect in respect of the undoped fuel is obtained on adding hydrogen sulphide to the mixture. The explanation advanced is that in conditions of high inlet temperature and high flame temperature due to high compression ratio, the exhaust valve and/or other not well cooled surfaces, such as the piston crown, are raised to the temperature required for the partial oxidation of the end gas to steam and carbon dioxide. The temperature is about 400° C. according to the experiments with a steel reaction chamber, see Fig. 12, and on inhibition of the reaction by hydrogen sulphide the pro-knock effect shown by the experiments would be expected.

A further interesting effect is shown by Graphs *E* and *F*, fig. 17. The graphs cross, showing that the hydrogen sulphide after destroying the antiknock effect of the dope and that due to oxidation of the fuel on hot surfaces carries on to give rise to a further pro-knock effect. The 'further' effect increases as the compression ratio is raised and flame temperature increased accordingly. This will be discussed in succeeding paragraphs.

Aviation Fuel Experiments.

The fuel was a high grade straight run Borneo petrol and when used undoped and with *unheated* induction the catalyst poisons were without the pro-knock effect which became evident when metallic dope was added. The experimental results given by the graphs of Fig. 18, obtained with an *induction temperature of 300° F.*, show the double effect already mentioned, that is, the hydrogen sulphide not only destroys the entire antiknock effect of the metallic dope but also the smaller similar effect attributed to the formation of steam and carbon dioxide on combustion chamber surfaces becoming active in the high temperature conditions. The two pro-knock effects obtained on adding hydrogen sulphide in a concentration of about 8% in the fuel suffice to reduce the octane number to 64.5.

Coal Spirit Experiments

The spirit was procured from the low temperature distillation of coal. The octane number was higher than that of the petrol but lead response was less; a 4 cc. per gal. addition of the metallic dope raised the octane number from 75½ to 84, whereas a similar addition to the aviation petrol raised the octane number from 70 to 85. The relatively low concentration of 3% of the hydrogen sulphide was sufficient to destroy the original antiknock effect of the dope, represented by an increase of 8½ octane numbers. The second and third

effects are as described for the engine experiments with hexane but are of greater magnitude and obtained with smaller percentages of hydrogen sulphide.

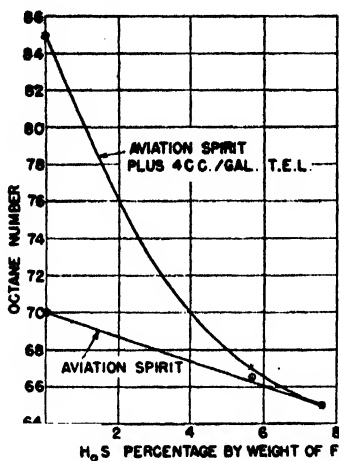


FIG. 18.

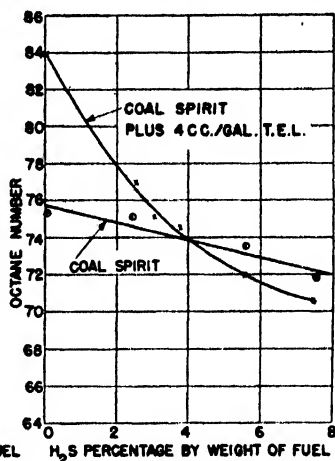


FIG. 19.

FIG. 18. Graphs showing the pro-knock effect of hydrogen sulphide on aviation spirit doped with tetraethyl lead. C.F.R. engine, 300° F. induction temperature.

FIG. 19. Graphs showing the pro-knock effect of hydrogen sulphide on coal spirit doped with tetraethyl lead. C.F.R. engine, 300° F. induction temperature.

Cyclohexane Experiments

The second and third pro-knock effects of hydrogen sulphide are shown by the engine experiments already described to become increasingly evident as the temperature of combustion is raised either by increasing compression ratio or by raising induction temperature. The experiments were, therefore, repeated in conditions requiring the use of compression ratios approaching the limit of the C.F.R. engine. Weak and rich mixtures of cyclohexane were used with induction temperatures of 300° F. and it will be seen by reference to the graphs of Fig. 20 that the highest useful compression ratios were 7.9, and 7.4 respectively in the circumstances. The H.U.C.R. values increased to 10.0 and 9.1 on adding tetraethyl lead to the fuel in the concentration of 24 cc. per gal. The excessive dope addition was used advisedly in an endeavor to determine whether the third pro-knock effect shown by the crossing of the graphs was due to the hydrogen sulphide or to the metallic dope in the presence of the sulphide. It is well known that the specific effect of tetraethyl lead diminishes as the concentration in engine fuel increases and it is probable that no more than one-third of the 24 cc. addition was effective to prevent detonation. The experimental results given by the graphs of Fig. 20 show that (a) The original increase in H.U.C.R. due to the dope was destroyed by about 5% of hydrogen sulphide in the weak mixture and about 2½% in the rich mixture.

(b) The second pro-knock effect of the hydrogen sulphide is more pronounced than in the experiments made at lower compression ratios. Thus the sulphide

in the concentration of 15% reduced the H.U.C.R. of the undoped fuel, weak mixture, from 7.9 to 6.2, that is, an amount equal to 80% of the increase obtained with the large addition of dope to the fuel in the absence of the catalyst poison. Similar effects were obtained for the rich mixture but comparisons cannot be made because the percentage of hydrogen sulphide added to the fuel-air mixture was not large enough to obtain limiting values for the effects.

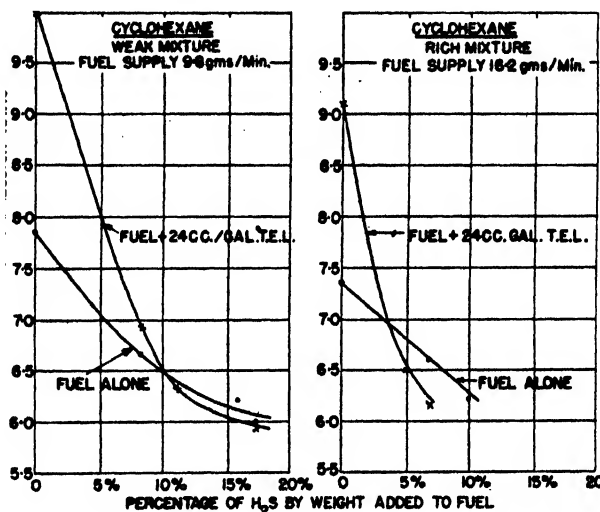


FIG. 20. Graphs showing the pro-knock effect of hydrogen sulphide on rich and weak mixtures. Cyclohexane doped with tetraethyl lead. C.F.R. engine, 300° F. induction temperature.

(c) The third pro-knock effect of the hydrogen sulphide, shown by the crossing of the graphs, is most apparent for the rich mixture for which fuel was supplied at the rate of 16.2 gm. per min. as compared with 9.8 for the weak mixture. The rich mixture in the engine contained, therefore, nearly twice as much dope as the weak mixture, and, since conditions in respect of hydrogen sulphide supply remained unchanged, it is reasonable to suppose that the third pro-knock effect was due in some way to the tetraethyl lead when used at high flame temperatures in the presence of the sulphide.

Benzene Experiments

The experiments with benzene as the engine fuel were undertaken to confirm that, as suggested above, tetraethyl lead becomes a pro-knock if used in conditions of high flame temperature and in the presence of hydrogen sulphide. It is well known that benzene does not detonate in the C.F.R. engine even when the compression ratio is as high as 10. The addition of metallic dope is, therefore, without apparent effect. Experiments were made accordingly at an induction temperature of 300° F. The experimental results are given by the graphs of Fig. 21. They show that when the undoped fuel was used at the high compression ratio of 10, detonation did not occur until hydrogen sulphide had been added to the mixture in the high concentration of nearly 20% by

weight of the benzene. This result confirms that the 'further' pro-knock effect observed in the earlier experiments was not due to the effect of the hydrogen sulphide alone. It will be noted, however, that on adding tetraethyl lead to the benzene in the concentration of 4 cc. per gal. detonation occurred

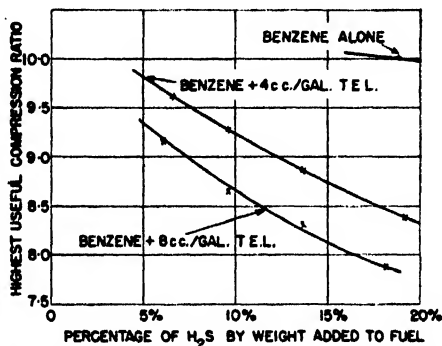


FIG. 21. Graphs showing the pro-knock effect of tetraethyl lead in small concentration in benzene obtained when combustion occurs in the presence of hydrogen sulphide. C.F.R. engine, unheated induction.

and the H.U.C.R. fell to 9.6 when the percentage of hydrogen sulphide in the fuel was 7% only, and further to 8.4 when the percentage was increased to 19. On increasing the concentration of tetraethyl lead to 8 cc. per gallon, a still greater pro-knock effect was obtained as shown by the lower graph of the figure, H.U.C.R. being reduced to 9.1 when the percentage of hydrogen sulphide was about 7, and to 7.8 when it was 18.

Section VI

DISCUSSION OF EXPERIMENTAL RESULTS

Nature of the Reactions Described

It was suggested, Section V, Part II (9), for discussion and further experiment "that the oxidation of pentane is an heterogeneous reaction, velocity depending on the nature of the contact surface and the manner in which the reacting mixture is brought into contact with it". Some further experimental work supporting the general proposition has been described in this Part and will be discussed in succeeding paragraphs.

When pentane is oxidized in reaction chamber No. 10, and the active surface is of clean Jena glass, the usual aldehyde hump appears on the graph for oxygen reacted, see Fig. 3. If now iron carbonyl be added to the reacting mixture, giving an active surface of iron, the aldehyde hump disappears and reaction is almost completely to steam and carbon dioxide (Graph B of the figure). Then on allowing the active surface to go to iron oxide by ceasing to supply the carbonyl, the aldehyde hump reappears (Graph C of the figure). These experimental results obtained with a flow configuration especially adapted rapidly

to remove oxidation products from the surface on which they are formed give strong support to the view that the oxidation reaction is heterogeneous.

The experiments with ethyl mercaptan give further support to the view mentioned. Thus, the graphs of Fig. 6 for the oxidation of hexane in the glass reaction chamber No. 10 in clean condition show that the aldehyde hump remains when ethyl mercaptan is added to the reacting mixture, indicating that the mercaptan is without effect to alter the surface at the temperature of the experiments. If, however, iron carbonyl be added to the reacting mixture instead of the mercaptan, Fig. 9, and an active surface of iron is deposited on the glass, the aldehyde hump disappears, and oxidation is to carbon dioxide and steam at all temperatures of reaction, as for pentane in similar conditions. If now the active iron surface is converted to the sulphide on adding the mercaptan, the aldehyde hump is not recovered and reaction velocity at all temperatures diminishes to a relatively low rate. The rate may reach zero at temperatures rising to over 500°C. and be inappreciable at higher temperatures in *suitable conditions of flow configuration* as shown by Graph B, Fig. 18, Part II (8). Again it is difficult to interpret the experimental results otherwise than by considering the reactions to be heterogeneous.

The experiments with the steel reaction chamber of relatively large volume, Fig. 12, are also significant. The surface was not of uniform temperature and was in part of iron oxide and in part of iron. The oxidation of pentane in the chamber is, therefore, a mixed reaction yielding, over the low temperature range, aldehyde on the oxide and final products on the iron. On adding ethyl mercaptan to the mixture, the reaction to aldehyde which occurs on the surface of iron oxide as previously shown, Fig. 3, continues but that to steam and carbon dioxide occurring on the iron part of the surface is inhibited, giving the over-all result as shown by the graphs of Fig. 12.

The Negative Temperature Coefficient of Reaction

The negative coefficient depends for its existence on the aldehyde hump which is more pronounced for oxidations in reaction chamber No. 10 than for oxidations in conventional combustion reaction spaces. It is necessary, therefore, in seeking an explanation to remember that in reaction Chamber No. 10 oxidation occurs with great rapidity, time of exposure being of the order of one second, that the high velocity of reaction is due to the flow configuration being adapted to remove surface oxidation products immediately on their formation, that the products do not remain in the chamber and on leaving it to reach the exit are exposed to temperatures lower than that of their formation. The chamber is thus suitable for following the course of reactions occurring at specified temperatures, and the existence of a negative temperature coefficient when pentane is oxidized in the chamber on other than a metal surface indicates that a reaction of high velocity is succeeded, on raising the temperature, by one of lower velocity. Thus referring to the graphs of Fig. 10, Part I (8), it will be seen that carbon monoxide formation reaches a maximum at about 400°C. , the temperature of the aldehyde hump,

and then falls to a minimum at 520° C. The rate of carbon monoxide formation then rises as temperature increases, slowly at first but with great rapidity at temperatures above 600° C. until at 660° C. it exceeds that of carbon dioxide formation. The experimental results show a high reaction velocity over the lower temperature range when the pentane is oxidized to aldehyde, and initially a relatively low reaction velocity at higher temperatures when the pentane is oxidized to carbon monoxide. During the temperature interval between the high velocity, low temperature reaction to aldehyde and the acceleration to high velocity of the high temperature reaction to carbon monoxide, the over-all rate of oxygen reacted reaches the relatively low value which accounts for the negative temperature coefficient. The oxidation of pentane could not proceed in the manner described if the reactions were homogeneous, so conversely the existence of a negative temperature coefficient may be taken as an indication of heterogeneous reactions.

A negative temperature coefficient of reaction was obtained by Pease (16) nearly 20 years ago and was observed when propane was oxidized by a flow method. The experiments of Pease and those of later workers are discussed by Jost in *Explosion and Combustion Processes in Gases*, pages 427-449, English translation by Huber O. Croft, and it is stated, page 449, that many facts support the conclusion that the reaction mechanism differs as between low and high temperature.

Oxidation in the End Gas in an Engine

If oxidation of the fuel in the end gas be a heterogeneous reaction, the anti-knock effect of metallic dope can be attributed to catalytic action, and detonation in the body of the gas cannot be due primarily to any process of oxidation. If, on the other hand, oxidation be a homogeneous reaction, existing theory in respect of the cause of detonation and the antiknock action of metallic dope would be supported. Antiknock action only will be discussed at present although some of the experimental work described in Parts I (8) and II (9) has an important bearing on the cause of ignition and detonation; a subject which it is proposed to discuss in a subsequent Part.

The Revised Positive Catalyst Theory

It is well established that the unburned combustible mixture (end gas) confined between the advancing flame and some part of the surface of the engine combustion space is the seat of detonation, that the *metal* of organo-metallic compounds is responsible for their antidetonation effect, and that turbulence is effective to reduce detonation. The temperature of the end gas in an engine not supercharged and using unheated mixture has been calculated to increase from 670° C. for a compression ratio of 4 to 880° C. for a compression ratio of 10, while the flame temperature may rise accordingly from 2500° to 2750° C., and radiation would be expected to give rise momentarily to high surface temperatures. The conditions as described, although prevailing for a small fraction of a second, suffice for at least partial oxidation of the end gas by flameless combustion. The experimental results for the

laboratory oxidation of doped pentane or hexane given by the graphs of Fig. 8, Part I (8), and Fig. 5 of this Part, in conditions of temperature, turbulence, and time of reaction approaching those prevailing in the combustion space of an engine, show that the metal of the dope deposited on the available surface effects the oxidation of the hydrocarbons to steam and carbon dioxide with great rapidity at temperatures above 500°C ., as long as the metal surface is maintained by continuous deposition from the organometallic compound. The end gas in an engine is always at a temperature higher than 500°C . late in the period of flame travel and the contact surface of the gas probably at a still higher temperature due to radiation from the flame. Doped fuel in the end gas would, in the circumstances, be oxidized with great rapidity to steam and carbon dioxide on the catalytic surface maintained as in the laboratory reaction chamber by continuous deposition of the metal of the dope. The effect of steam especially to reduce inflammability is shown by the experiments described in Section I, and, dilution of the end gas being sufficient, self-ignition ahead of the flame could not occur and combustion would be completed in the normal course without detonation. Verification that the action of metallic dope is as described is obtained by considering the effects of sulphur compounds which are catalytic poisons in respect of the carbon dioxide-steam reaction on metal surfaces. Thus, ethyl mercaptan inhibits the carbon dioxide-steam reaction in laboratory oxidations of doped fuels, as shown by the experiments described in Section IV, and the mercaptan or hydrogen sulphide, when added to doped engine fuel, destroys the antiknock effect of the organometallic compounds as shown by the experiments described in Section V. When hexane undoped was used as fuel in the C.F.R. engine in conditions leading to relatively low flame and engine temperatures, the catalytic poison was of no pro-knock effect even in the large concentration of 15% in the fuel, Graph C, Fig. 17. However, when conditions of engine operation led to relatively high surface temperatures in the combustion space, the consequent steam-carbon dioxide reaction became an antiknock factor because knock occurs on its inhibition by the catalyst poison (see Figs. 18, 19 and 20). The antiknock effect of hot surfaces is most evident at high compression ratios which are necessarily accompanied by correspondingly high flame temperatures. Thus, referring to Fig. 20, inspection of the graphs shows the decrease in H.U.C.R. obtainable by inhibition of the carbon dioxide-steam reaction to be almost as great as the increase obtained on the addition of tetraethyl lead in very large concentration. That is, the tetraethyl lead antiknock effect is added to an existing effect. Both effects are due to dilution of the end gas with the product of a carbon dioxide-steam reaction and both are destroyed by the catalyst poison.

Acknowledgments

In addition to the acknowledgments made in Part I, in respect of the experimental work carried out in the Colloid Science Laboratory, Cambridge, thanks are due to Dr. George Mole for assistance with the experiments on

the oxidation and ignition of hydrogen described in Section I and to Dr. H. Moss and Mr. W. J. Stern for assistance with the engine experiments described in Section V.

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NOTICE

Sections "A" and "B" for March 1948 will be mailed at a later date.

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THE PAPER MAKING PROPERTIES OF STRAW HOLOCELLULOSE¹

BY G. A. ADAMS² AND A. E. CASTAGNE³

Abstract

Fibrous holocellulose pulps were prepared in approximately quantitative yield from flax shives and wheat, oat, and fiber flax straw that had been macerated in a buhrstone mill and delignified by sodium chlorite. Paper hand sheets that were formed from pulps subjected to prolonged beating were glassinelike in character. Strength of all straw holocelluloses developed slowly on beating. All papers had relatively low densities compared with the usual values for papers from wood pulps. Tear resistance was initially low for all straw holocelluloses, especially flax shives, and decreased with beating. Color reversion, due almost entirely to light, was rapid in all test sheets. Possible uses for straw holocellulose papers are suggested, although, at present, the process is too expensive to be commercially feasible.

Introduction

Recent methods of preparing holocellulose in quantity have permitted investigation of the physical characteristics of papers containing the entire carbohydrate fraction of the cell wall (1, 8, 14, 16). Retention of the hemicellulose fraction of wood greatly increases the yield of pulp without impairing its paper making qualities. Jayme *et al.* (6) have made test sheets of good mechanical properties from aspen holocellulose. Studies on spruce holocellulose by Houtz and Kurth (5) showed that the presence of polyuronide hemicelluloses and cellulosans led to the development of a gelatinous hydrate on beating, and the glassine-type paper formed had remarkable strength characteristics. Investigation of white spruce holocellulose by Hajny and Ritter (3) showed that it had a high content of undegraded alpha-cellulose. They recommended removal of the hemicellulose fractions to give pulps with the desired characteristics for any particular purpose. Contrary to the statement of Holmberg and Jahn (4) that a true holocellulose cannot be prepared from softwoods, Lovell (8) has reported preparation of holocellulose from hemlock and slash pine with only slight loss. While holocelluloses from nonwoody plant materials have been prepared by methods involving acid chlorite (1, 2), chlorine-ethanolamine (11), and chlorine-pyridine (17), only Schenck and Kurth (11) have made a study of the paper making properties of holocellulose isolated from wheat straw. The straw holocellulose, unlike that of wood, developed strength very slowly on beating. No study has been found of the paper making properties of straw holocellulose prepared by the acid chlorite procedure.

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The present paper deals with an investigation into the preparation of four straw holocelluloses by the acid chlorite method, their conversion to pulp stock and paper sheets, and an evaluation of the paper quality by physical tests. Wheat, oat, and flax straws were investigated because they are the commonest types and readily available; flax shives were studied because they are a by-product for which uses are being sought.

Experimental and Results

Raw Materials

Sound mature wheat and oat straws threshed from the 1946 crop were used. Owing to handling, most of the loose chaff and broken particles were absent from these straws. Occasional heads and kernels were removed by hand. Fiber flax was carefully freed of head and root structures. Flax shives were used directly as received from a flax processing plant. All materials were analyzed for moisture, lignin, ash, and Cross and Bevan cellulose by standard TAPPI methods (12). The results are given in Table I, A.

TABLE I
COMPOSITION OF STRAWS AND THEIR HOLOCELLULOSE FRACTIONS, % (ALL MATERIALS REPORTED ON AN OVEN-DRY BASIS)

	Wheat	Oats	Fiber flax	Flax shives
<i>A. Straw</i>				
Lignin (ash free)	21.21	19.21	22.54	30.11
Ash	6.89	8.95	3.52	1.46
Cellulose	54.9	49.6	52.4	48.2
*Hot water solubles	10.22	12.87	11.03	2.13
<i>B. Holocellulose</i>				
Yield	77.9	80.2	79.2	72.8
Lignin (ash free)	2.46	2.37	4.05	4.80
Ash	4.17	2.62	3.11	3.92
Cellulose	74.9	75.1	70.1	68.0

* Extraction temperature, 75° C.

Mechanical Pulping of Straw

Mechanical pulping of the straws was necessitated by the failure of acid chlorite delignification to effect any separation of cellulose fibers as occurs in most chemical pulping procedures. Acid chlorite holocellulose retains the physical characteristics of the original straw and cannot be satisfactorily pulped by the usual beater treatment. Preliminary mechanical pulping of the straws by maceration in ball mills, rod mills, and Waring blenders was not satisfactory owing to formation of a high proportion of fines and lack of break-down of nodular structures. Test sheets of paper made from pulps prepared by these means contained an objectionable number of 'shives'. It was found that a buhrstone mill shredded the straw to a relatively fine fibrous pulp.

The pulping procedure finally evolved was as follows. About 1500 gm. of air-dry straw was chopped into pieces about $\frac{1}{2}$ to 1 in. in length by means of a

commercial feed cutter. The cut straw was then steeped for four to five hours in 30 liters of water at 75° C. to promote softening for the milling operation and to remove dirt particles and water soluble materials. The steep water was removed by straining through cloth and the straw was thoroughly washed. The wet material was then fed directly by hand into a 36 in. buhrstone mill. Clearance of the moving stone during milling was adjusted arbitrarily to produce a uniform pulp. Water at the rate of 4 to 5 liters per min. was fed in with the straw. The pulp was recovered on a 48 mesh screen, and squeezed out, and recovered by hand. Owing to lack of proper screening equipment, the loss of fiber in the milling operation was about 15 to 20% of the straw. The wet pulp was not allowed to dry out before being delignified.

Preparation of Straw Holocellulose

The method used for preparation of holocellulose was an adaptation of Wise's analytical procedure using acid chlorite (16) and has been described previously by the authors (1). The wet pulp was diluted to a consistency of 5% with water and subjected to delignification treatments for one hour at 75° C. using 30 gm. of sodium chlorite and 2.4 ml. of glacial acetic acid per 100 gm. of dry straw pulp. Three successive treatments were used for wheat and oat straw; five were necessary for fiber flax and shives. The pulps were then freed of their solutions by spinning in a perforated centrifuge bowl lined with fine filter cloth, and washed with distilled water until chloride-free. They were stored in the wet state until made into paper. The yields of crude holocellulose and their lignin, ash, and cellulose contents are given in Table I, B.

Beater Tests

The holocellulose pulps were diluted to a 1.5% consistency and processed in a 1.5 lb. standard laboratory type Valley beater. Preliminary tests showed that the usual side arm loading caused too drastic cutting action on the fibers so all experiments were done with 1 kgm. loadings. Samples were withdrawn at 10 min. intervals for freeness tests according to TAPPI Standard T227 m-46. Hand sheets were prepared for physical tests and optical tests by TAPPI standards T205 m-45 and T218 m-46 respectively.

Physical Tests on Paper

The hand sheets were conditioned for 24 hr. at 70° F. and 50% relative humidity according to TAPPI Standard T402 m-44. The physical properties that were determined by TAPPI Standard T220 m-46 were as follows: basis weight, density, burst factor, tear factor, and breaking strength. The thickness of four sheets was measured with a Schopper automatic micrometer (accurate to 1/1000 in.) and the results divided by 4. Printing opacity, which is the ratio of R_1 , the reflectance of a single sheet backed with black, to R_s , the reflectance of a pile of sheets, was determined with a General Electric reflection meter. The observed readings for the various sheets were calculated to a standard sheet weight of 1.2 gm. Brightness was measured with a General Electric reflection meter according to T452 m-42. The results of the physical tests are given in Tables II, III, IV, and V.

TABLE II

PHYSICAL PROPERTIES OF PULP MADE FROM WHEAT STRAW HOLOCELLULOSE

Beating time, min.	Freeness, (Canadian standard), ml.	Basis wt. gm./sq. m.	Density, gm./ml.	Burst factor, gm./sq. cm./gm.	Tear factor, 100 X gm./gm.	Breaking length, m.	Printing opacity $\frac{R_1}{R_2}$	G.E. brightness at 458 m μ , %
0	724	70.3	0.43	10.6	40.9	3909	0.750	66.1
10	677	67.0	0.45	12.3	38.1	4259	0.816	68.2
20	669	68.7	0.49	18.2	36.1	4573	0.765	68.4
30	560	71.3	0.53	20.8	33.4	5358	0.709	65.2
40	550	70.0	0.56	28.2	33.5	6631	0.820	62.2
50	520	68.2	0.58	31.3	33.4	7171	0.881	65.4
60	473	68.5	0.62	36.2	28.0	7293	0.800	63.1
70	448	68.5	0.64	41.3	28.0	7345	0.830	65.3
80	429	68.2	0.65	43.5	27.3	7852	0.852	61.3
90	344	69.3	0.69	44.5	26.7	8082	0.661	61.6

TABLE III

PHYSICAL PROPERTIES OF PULP MADE FROM OAT STRAW HOLOCELLULOSE

Beating time, min.	Freeness, (Canadian standard), ml.	Basis wt., gm./sq. m.	Density, gm./ml.	Burst factor, gm./sq. cm./gm.	Tear factor, 100 X gm./gm.	Breaking length, m.	Printing opacity $\frac{R_1}{R_2}$	G.E. brightness at 458 m μ , %
0	706	66.1	0.50	8.8	36.0	3463	0.736	61.6
10	677	67.0	0.45	12.8	39.7	4259	0.780	62.1
20	635	66.5	0.50	15.5	38.5	4558	0.820	62.4
30	607	65.4	0.46	15.8	37.4	4638	0.792	62.3
40	592	65.2	0.50	19.3	35.4	5579	0.740	62.2
50	565	64.9	0.50	21.3	34.3	6101	0.680	61.8
60	514	65.6	0.55	26.6	32.6	6204	0.724	60.5
70	485	65.2	0.56	30.8	30.5	6837	0.746	60.2
80	447	64.7	0.62	34.9	27.4	7715	0.680	56.9

TABLE IV

PHYSICAL PROPERTIES OF PULP MADE FROM FIBER FLAX HOLOCELLULOSE

Beating time, min.	Freeness, (Canadian standard), ml.	Basis wt., gm./sq. m.	Density, gm./ml.	Burst factor, gm./sq. cm./gm.	Tear factor, 100 X gm./gm.	Breaking length, m.	Printing opacity $\frac{R_1}{R_2}$	G.E. brightness at 458 m μ , %
0	466	68.0	0.26	4.5	47.0	1731	0.880	70.9
10	374	70.6	0.33	6.6	47.3	2528	0.795	67.2
20	289	69.6	0.35	8.3	40.3	3075	0.802	67.5
30	221	69.6	0.39	10.4	37.2	3331	0.810	69.0
40	176	71.3	0.38	11.0	37.8	3755	0.874	66.9
50	128	67.2	0.42	13.6	31.2	5045	0.887	67.0
60	98	72.4	0.45	15.6	27.5	5175	0.820	57.6
70	68	65.9	0.46	17.0	22.1	5415	0.848	62.4
80	53	64.6	0.51	20.8	24.8	5414	0.632	64.0

TABLE V

PHYSICAL PROPERTIES OF PULP MADE FROM FLAX SHIVES HOLOCELLULOSE

Beating time, min.	Freeness, (Canadian standard), ml.	Basis wt., gm./sq. m.	Density, gm./ml.	Burst factor, gm./sq. cm./gm.	Tear factor, 100 X gm./gm.	Breaking length, m.	Printing opacity $\frac{R_1}{R_x}$	G.E. brightness at 458 m μ , %
0	448	65.4	0.34	6.9	19.0	1746	0.848	70.8
10	368	67.5	0.38	8.8	18.4	2272	0.854	71.1
20	313	67.2	0.41	12.3	17.4	2974	0.894	69.0
30	282	67.2	0.47	15.2	15.4	3505	0.846	68.8
40	272	67.0	0.50	17.2	14.8	3992	0.801	68.8
50	262	66.2	0.53	19.3	15.0	4149	0.850	66.3
60	232	67.7	0.53	19.6	13.6	4323	0.861	65.4
70	218	66.5	0.56	21.9	13.8	4558	0.846	62.0
80	196	69.0	0.63	23.4	12.9	4914	0.790	64.3

All papers were of the glassinelike type after about 50 min. of beating and resembled, in general, papers made from wood holocellulose.

With increase in beating time, the drop in freeness of all pulps was progressive and slow. Fiber flax holocellulose gave the greatest decrease in freeness and the pulp eventually became almost gelatinous. Since hemicellulose fractions are known to increase chemical hydration of pulps (5, 10), it was undoubtedly their presence rather than cutting and fibrillation of the cellulose fibers that contributed to the loss of freeness on beating. The rather light beating treatment used was also a factor in prolonging freeness; however, drastic beating was found to cause excessive cutting of fibers and poor felting qualities in the pulp. The low initial freeness of flax pulp in comparison with that of wheat and oats indicated quite different hydrating properties.

Development of bursting strength was also slow and did not reach a maximum for any pulp in 80 min. Similar results have been reported by Schenck and Kurth (11) for wheat straw holocellulose prepared by the chlorination-ethanolamine procedure. They attributed the slow strength development to the presence of silica in wheat holocellulose. However, this explanation does not appear to be satisfactory, since it was shown in the present work that slow strength development was characteristic of all holocelluloses tested, even though the silica content of wheat holocelluloses was 2.05%, oat 1.14%, and flax nil. Straw holocellulose appeared to exhibit a behavior fundamentally different from that of wood holocellulose, which develops strength rapidly on beating (3, 5). Lovell (8) found, however, that the bursting strength of slash pine holocellulose was high initially and did not increase further. A relatively short beating time of 15 min. was used and there was an extremely sharp drop in freeness. The presence of the hemicellulose fractions is known to increase the hydration of the pulp and contribute to bursting strength. The exact role of the pentosans in binding the cellulose fibers together is unknown but is believed to be a combination of physical and chemical bonding (9, p. 53; 13).

Progressive increase in density with beating was shown for all straws except oats, the increase being greatest in flax. Decrease in bulk in beating pulps is due to a combination of collapse of fibers, partial breaking of fibers, and filling in of the air spaces. Although the crushability of the cellulose fibers was a factor in bulk decrease, the main effect was due to the disintegrating action of the beater. The relatively low densities of straw holocellulose pulps compared with wood should make them useful as 'fillers' in certain kinds of papers made from wood pulp.

The tear strength of all pulps decreased steadily with beating time; this indicated that the fiber lengths were being shortened. Loss of tear strength has been claimed also to indicate ease of hydration. Wood holocellulose from which various hemicelluloses—the easily hydrated fraction of wood—had been removed, showed a progressive resistance to tear (5). The relatively high initial tear resistance of fiber flax holocellulose was due, probably, to the presence of a considerable proportion of coarse fiber bundles in the pulp. The lack of uniformity of texture in the test sheets contributed to low bursting strength and high tear resistance. Flax shives, which consist of relatively short fibers, showed a minimum of tear resistance.

Tensile strength increased with beating for all pulps and indicated progressive increase in fiber-to-fiber bonding. The flax pulps increased steadily in tensile strength over the beating period while wheat and oat straws showed most rapid gain in strength after 20 to 30 min. of beating.

Changes in printing opacities with increased beating time were small and showed little in the way of trends. Lack of uniformity in the formation of many sheets contributed to the irregular results. The only marked decreases in printing opacities were shown after 80 min. of beating (90 min. for wheat holocellulose); this change in property can be correlated with a rise in density for the same beating period. However, no general correlation existed between the progressive increase in density over most of the beating period and printing opacities. Schenck and Kurth (11) have reported little change in opacity (contrast ratio) of wheat straw holocellulose on increased beating.

All brightness values were low when compared with those of bleached wood pulps, which usually are in the range 80 to 90. A slight tendency for brightness to increase with beating time was noted. The brightness of all pulps was much higher than those previously reported for sheets of wheat straw holocellulose (11).

Aging of Straw Holocellulose

Hand sheets made from the straw holocelluloses were observed to undergo color reversion on exposure to light and drying temperatures (90° C.). Houtz and Kurth (5) demonstrated that papers containing hemicellulose fractions aged more rapidly on exposure to ultraviolet light than high alpha-cellulose papers. Rapid color reversion with loss of brightness was found in wheat holocellulose papers by Schenck and Kurth (11).

Quantitative measurement of the 'aging' effect of light was obtained by accelerated tests in a fadeometer. Hand sheets prepared from wheat, oats, and flax pulps that had been beaten for 30 min. were exposed to ultraviolet light from a carbon arc in a humidified fadeometer. The relative humidity was 25% and the temperature 33° to 34° C. Brightness measurements were made on a General Electric reflection meter after various time exposures. The results are given in Table VI. All papers showed a marked loss in bright-

TABLE VI

EFFECT OF AGING BY ULTRAVIOLET LIGHT ON PAPER MADE FROM VARIOUS STRAW HOLOCELLULOSES

Exposure time, hr.	Brightness, %			
	Wheat	Oats	Fiber flax	Flax shives
0	62.1	58.9	66.9	68.6
1	53.9	53.4	57.9	57.9
2	52.0	53.2	54.8	53.5
4	50.4	49.5	54.1	52.3
6	50.5	49.8	50.9	52.4
8	48.9	49.1	50.9	50.3
12	46.9	46.4	48.2	47.2

ness after one hour's exposure. Thereafter the decrease was much more gradual. The actual loss in brightness was greater for flax straws than either wheat or oats and all losses were much greater than is commonly found in bleached papers from wood pulp.

Since the temperature in the fadeometer was considerably higher than ordinary room temperature, the effect of heat had to be taken into account. Four sheets of each paper were covered with two layers of photographic 'light proof' paper and exposed under the previous conditions for 12 hr. Four uncovered sheets of each paper were exposed to ultraviolet light for the same length of time. The results given in Table VII show that most of

TABLE VII

EFFECT OF AGING BY ULTRAVIOLET LIGHT AND HEAT ON PAPERS MADE FROM VARIOUS STRAW HOLOCELLULOSES

Conditions	Exposure time, hr.	Brightness, %			
		Wheat	Oats	Fiber flax	Flax shives
Control	0	62.1	58.9	66.9	68.6
Heat	12	60.3	58.1	65.1	67.4
Light + heat	12	46.9	46.4	48.2	47.2

the loss of brightness in all papers was due to the effects of light rather than heat. Launer and Wilson (7) have shown that lignified papers are very unstable to light, especially in the presence of oxygen. Since the holocellulose

contained as high as 4.8% apparent lignin, it may be that the lignin rather than the hemicellulose was responsible for the yellowing. It is significant that the flax papers, which contained more lignin than either wheat or oats, showed the greatest light aging effects.

Uses for Holocellulose Papers

Holocellulose pulps are worthy of commercial interest because of their high yields from woods and straws. Ordinarily about 40% of wood or straw is recovered as useful chemical paper stock, while holocellulose yields are of the order of 65 to 70% of the original material. Most of the gain is due to retention of the hemicellulose fraction but a lesser part comes from quantitative preservation of the alpha-cellulose fraction (5). Paper sheets of the glassine type with good physical properties can be readily made. Further chemical treatments can be used to remove hemicellulosic fractions and ultimately yield pure alpha-cellulose. Studies along such lines have already been carried out on wood and sufficiently pure cellulose for the making of derivatives has been obtained (15).

Holocellulose pulps might find uses as glassine or parchment-type papers. Admixture with a proportion of wood pulp with long fibers would make papers such as bond, where hardness, stiffness, and rattle are of value. Additional bleaching would overcome the difficulty of rapid aging. The low density of the straw holocellulose papers would make them valuable as fillers in printing sheets and paperboard. Low tear resistance prohibits their extensive use in paper bags. However, there is little doubt that holocellulose stock would be used in all branches of the paper industry if the cost were competitive with present materials.

At the present time, the cost of making holocellulose by the acid chlorite method is prohibitive owing to the high cost of sodium chlorite. If the price of this chemical could be reduced to about one-quarter of its present figure, then holocellulose pulps would become of immediate interest. No doubt the process would be applied first to wood, because, when available, wood possesses well known advantages over straw as a raw material for pulping.

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EFFECT OF PROCESSING AND STORAGE ON THE QUALITY OF GELOSE FROM IRISH MOSS (*CHONDRUS CRISPUS*)¹

BY D. MACDOUGALL²

Abstract

Irish moss (*Chondrus crispus*) from Canada's east coast was used to study possible improvements in the production and storage of gelose. The optimum pH for the extraction of gelose from Irish moss was between 6 and 7. Fine leaf particles, which prevent rapid filtration, were readily removed by supercentrifuging. Comparison of drum drying and drying from the frozen state showed that the former caused a marked lowering of viscosity but had little effect on suspending power or jelly strength. The logarithm of the viscosity determined by means of a MacMichael viscosimeter was related directly to the concentration; therefore, viscosity measurements can be corrected for the moisture content of the samples. The effect of storage temperature on deterioration was greater than the effect of relative humidity. Samples stored at 0° and 40° F. for 12 weeks showed no significant changes in viscosity or suspending power, whereas those stored at 80° and 120° F. deteriorated very rapidly. Material was vacuum ice-dried to 2% moisture without damage but the quality decreased when the extracts were stored at high temperatures.

Introduction

The principal use of the water soluble carbohydrates of Irish moss (*Chondrus crispus*) is in the dairy industry where it serves as a suspending agent in the manufacture of chocolate milk. It also finds considerable use in the pharmaceutical industry as a stabilizer for emulsions and suspensions. In addition to these it serves as a sizing agent in the textile industry, a clarifying agent in the manufacture of beer, a thickener for cold water paints, and a gelling agent in desserts.

Prior to 1939, the bulk of the Irish moss (*C. crispus*) used on this continent was imported from Europe. When this source of supply was cut off by the European war, agar-agar from Japan was substituted where possible. The entry of Japan into the war forced Canada to seek domestic sources of gelling material. Irish moss was available in quantity on Canada's east coast and the processing of this product was examined in these laboratories (2, 6). However, some commercial processors noted that stored dried extracts deteriorated in certain attributes. This paper describes an examination of some of the processing operations and storage conditions that might have affected storage stability.

Analytical Methods

Moisture was determined by drying in air for 16 hr. at 212° F. pH was determined with a Leeds and Northrup pH meter.

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A number of methods were tried to establish possible criteria of quality. Reducing sugars (5), free sulphate (8, p. 613), and determination of the gelose content of extracts with benzidine (3) all showed little difference between fresh and stored extracts. Fluorescence values were also useless. However, the commonly used criteria, suspending power, viscosity, and jelly strength, were all found to be useful. The relation of these properties to the uses listed above is obvious.

Suspending Power

The minimum weight, in grams, of dried gelose extract required to give perfect suspension of cocoa in milk was used as an index of suspending power. In the procedure used, various amounts of the dried extracts were weighed into quart cans and 500 gm. milk (2% butterfat), 31.5 gm. sugar, and 5.8 gm. cocoa were added. The containers were closed with screw caps, blocked in a churn, and rotated end over end at about 20 r.p.m. for five minutes at room temperature to mix the ingredients. The churn was then filled with boiling water and rotated for 20 min. The hot water, now about 158° F., was removed, and the milk cooled by two five-minute churnings in water at about 41° F. The contents of the cans were then strained through 80 mesh screens (U.S. Bureau of Standards) into pint milk bottles which were held for 16 to 20 hr. at 40° F. and then for four hours at room temperature.

A suggested alternative method for determining suspending power, described by Rice (7), was examined and found unsatisfactory. Repeated attempts failed to give reproducible results. Rice states that the method is inaccurate in the presence of neutral salts and this may explain some of the difficulty, as these tests were made on commercial material whereas Rice used highly purified extracts. The method is even more cumbersome than the chocolate milk procedure because of the larger number of laboratory manipulations, and numerous attempted modifications to make it more easily applicable were unsuccessful.

Other tests of suspending power were tried but bore no relation to the chocolate milk test. These included: gold numbers (4, p. 58); stabilization of a standard ferric oxide solution against the precipitating action of sodium sulphate; and measurement of the precipitated cocoa in conical-bottomed centrifuge tubes.

Viscosity

The viscosity was determined in a MacMichael viscosimeter with the cup rotating at 20 r.p.m. A portion of dried moss extract (4.00 gm.) was dusted into 200 ml. of distilled water and the mixture was heated in a boiling water bath for 10 min. with stirring. The sol was made up to its original weight with distilled water, and was cooled to 140° F. The viscosity was then determined. All viscosity values are expressed in MacMichael units.

The moisture content of air-dried extract varied from 2 to 30% depending on the relative humidity at which the material was stored. It was, therefore, necessary to correct for the moisture content of each sample so that the values

for all determinations could be brought to a common basis. The concentration-viscosity relation was investigated on several different lots of material. Statistical analysis of the results indicated that a correction factor of 0.3940 units of log viscosity for each additional gram of dry matter was generally applicable. This formula was further tested on several lots of commercial material, with the results shown in Fig. 1.

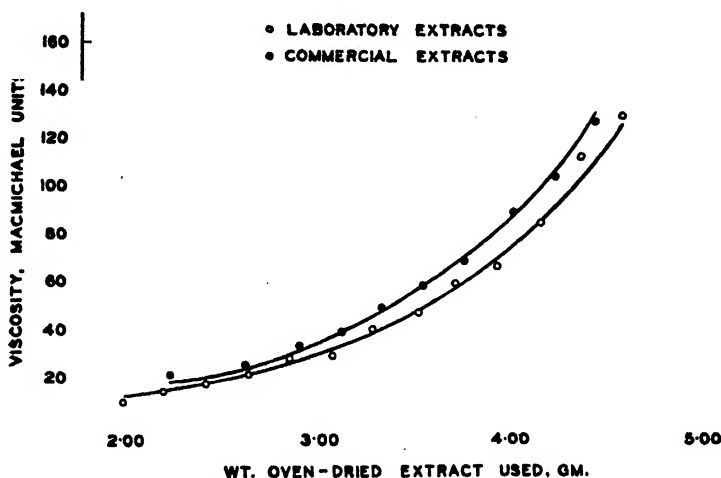


FIG. 1. The relation between viscosity and concentration of oven-dried extracts of Irish moss.

Jelly Strength

The method of preparation of the material was similar to that for the viscosity test except that 1.50 gm. of dried extract and 100 ml. of distilled water were used and the sample was cooled to 40° F. and held there for 16 hr. Jelly strengths were determined at this temperature with a Hall gelometer. All values are expressed in Hall units, which vary inversely with the jelly strength.

The Effect of Some Processing Procedures on Quality

pH of Extraction Medium

Buffer solutions (10 liters) 0.05 *M* with respect to phosphate and ranging in pH from 5.3 to 8.0, prepared as described by Clark (1, p. 81), were used to extract 300-gm. samples of fully bleached Irish moss. The extracts were dried from the frozen state (2), ground, and tested. Results of the experiment are contained in Table I. pH had little effect on the percentage of gelose in the extracts obtained, but because the more acid solutions gave less viscous sols, separation from the leaf residue was more complete and higher yields were obtained from these. There was little effect of pH on suspending power. Buffer solutions of pH 5.3 and 5.6 resulted in a material with poor viscosity when made into sols, and solutions of pH 7.4, 7.8, and 8.0 gave materials that formed gels too weak to be measured. Therefore, the pH for optimum viscosity lies between 6 and 7.

TABLE I

EFFECT OF pH OF EXTRACTING SOLUTION ON THE QUANTITY AND QUALITY OF GELOSE EXTRACTED FROM IRISH MOSS

pH of extraction solution	Yield, %	Solids in extract, %	Minimum conc. giving complete suspension, gm.	Viscosity of product, MacMichael units	Jelly strength, Hall units	pH of jelly
5.3	43	2.2	0.28	3	2.2	6.0
5.6	51	2.4	0.27	4	2.1	6.1
6.0	38	2.1	0.28	8	1.9	6.2
6.3	28	1.8	0.26	12	1.7	6.3
6.5	28	1.8	0.28	9	2.0	6.5
6.7	29	1.8	0.30	14	2.2	6.7
6.8	26	1.8	0.30	17	1.8	6.8
7.0	32	1.9	0.30	16	2.4	7.0
7.2	26	1.8	0.35	17	2.1	7.1
7.4	25	1.8	0.30	17	—	7.4
7.8	27	2.0	0.34	24	—	7.6
8.0	28	1.9	0.30	11	—	7.6

Separation of Leaf Fragments

Fulton and Metcalfe (2) suggested the use of a countercurrent extractor to increase the solid content of the gelose solution. However, they were obliged to extract twice to obtain a satisfactory yield of gelose, because, if the leaves were filtered under pressure, many fine leaf fragments remained in the extract and these prevented subsequent filtration. Basket centrifuging did not remove them.

However, the Sharples supercentrifuge was capable of removing a sufficient number of the tiny leaf fragments to render filtration easier. The present procedure consisted of two steps: drainage through a 40 mesh screen (U.S. Bureau of Standards), followed by air pressure filtration (10 lb. per sq. in.). As much of the clear liquid as would readily drain from the leaves was removed first and set aside. Then the portion obtained by pressure filtration was heated to about 194° F. and blown through the supercentrifuge at a rate of 0.3 liter per min. The centrifuged liquid was then combined with the drained liquid before treatment with charcoal and filter-aid (Johns-Manville No. 545). The resulting solutions were clear, odorless, and tasteless, and the yield was as high as that with the countercurrent extraction method (2).

Drying

Since commercially available moss extracts are usually dried on steam heated drums, a comparison was made between material prepared by the freeze drying method developed in these laboratories (2) and material prepared on a laboratory double-drum drier (steam pressure in the drums, 50 lb. per sq. in., gauge). For both tests the starting material consisted of a sol of Irish moss gelose containing potassium chloride and with a solids concentration

of 4%, obtained by adding previously dried extract. At this concentration, the material dried from the frozen state had fewer ice crystals embedded in the partially dehydrated sheet and it was unnecessary to place crushed ice on the jelly to prevent supercooling.

The results, given in Table II, show that material dried from the frozen state is very little better than drum dried material as a suspending or jelling agent, but that the former produces sols with much greater viscosity. This

TABLE II

QUALITY TESTS ON DRUM- AND FREEZE-DRIED EXTRACTS OF IRISH MOSS GELOSE, STORED AT 40° F.

Drying method	Storage time, days	Moisture, %	Jelly strength, Hall units	Suspending power, gm.	Viscosity, MacMichael units
Drum	0	12.0	1.20	0.22	15.5
	15	11.5	1.25	0.20	16
Freeze-dried	0	16.0	1.25	0.17	59
	15	15.0	1.30	0.19	44

finding, together with the results given under "pH of Extraction Medium", indicates that suspending power is a relatively stable property of Irish moss gelose, and that viscosity values are not related to indices of suspending power.

The Effect of Storage on Quality

In this experiment both dried extracts prepared in this laboratory and samples of commercial material were studied. Samples were stored at 0°, 40°, 80°, and 120° F. in relative humidities of 0%, 30 to 40%, and 70 to 75%. Each batch was sampled after 1, 2, 4, 8, and 12 weeks of storage.

In view of the variability of the data on viscosity and suspending power, they were transformed to logarithms, plotted against logarithms of time in weeks, and the slopes b of the best fitting straight lines were determined. The regression coefficients and their necessary differences are shown in Table III. There was no significant decrease in the viscosity of the samples stored at 0° and 40° F. However, there was a significant decrease in the viscosity of all samples stored at 80° and 120° F. In the samples stored at 120° F. the relative humidity had significant effects on the rate of viscosity loss. The suspending power did not change during storage at the lower temperatures, the only significant difference being at 120° F. and high relative humidity.

After 12 weeks' storage the reducing sugar (5), free sulphate (8, p. 613), and final moisture contents of each of the storage batches were determined. The pH of 2% solutions of material stored at 0° and 120° F. was also determined. No reducing sugar was found in any of the samples. The results of the remaining measurements, given in Table III, show that free sulphate was

TABLE III

THE QUALITY OF SAMPLES OF IRISH MOSS GELOSE STORED FOR 12 WEEKS AT VARIOUS TEMPERATURES AND RELATIVE HUMIDITIES

Criteria	Storage Temperature, °F.	0% R.H.*	30-40% R.H.*	70-75% R.H.*	Necessary difference, 5% level
Average decrease of log viscosity per log week, <i>b</i>	0	0.08	0.00	0.04	0.11
	40	0.02	0.01	0.10	
	80	0.19	0.19	0.26	
	120	0.47	0.62	0.76	
Average increase of log suspending power index per log week, <i>b</i>	0	0.05	0.04	0.03	0.16
	40	0.04	0.01	0.01	
	80	0.06	0.10	0.11	
	120	0.12	0.12	0.17	
Final pH, done on 2% solutions	0	5.4	5.5	6.1	—
	40	—	—	—	
	80	—	—	—	
	120	4.9	5.2	5.0	
Final free sulphate content, p.p.m.	0	Trace	Trace	0	—
	40	Trace	0	Trace	
	80	Trace	0	0	
	120	2,690	3,070	4,560	
Final moisture content, %	0	8.5	13.8	23.9	
	40	3.7	12.0	22.2	
	80	1.1	13.9	21.3	
	120	1.0	13.2	21.9	

* Relative humidity.

found only in material stored at 120° F., and that solutions of material stored at 120° F. were more acid than solutions of material stored at 0° F. With the exception of samples stored at 0% relative humidity and at the lower temperatures, moisture content had apparently reached equilibrium during the 12 week storage period. Relative humidity had important effects on moisture content and should preferably be kept below 50% relative humidity. In general, storage temperatures of 80° F. or higher caused some deterioration while temperatures of 40° F. or lower were satisfactory.

Samples of commercial material were stored under atmospheres of air, oxygen, and nitrogen at 140° F. and at relative humidities of 0% and 70 to 75%. These were tested at various intervals and the results, given in Table IV, show that there was little difference in the rates at which the samples deteriorated.

TABLE IV

EFFECTS OF STORAGE UNDER DIFFERENT ATMOSPHERES AT 140° F. ON IRISH MOSS GELOSE

Atmosphere	0% R.H.			70 to 75% R.H.		
	Storage time, days	Viscosity, MacMichael units	Suspending power, gm.	Storage time, days	Viscosity, MacMichael units	Suspending power, gm.
Air	0	22.5	0.25	0	22.5	0.25
	3	13.5	—	6	4.5	—
	10	6.0	0.40	12	3.5	—
	20	6.0	—	17	2.5	—
	34	4.0	0.60	20	2.5	0.65
Ox. gen	0	22.5	0.25	0	22.5	0.25
	3	12.5	—	6	4.5	—
	10	8.0	—	12	2.5	—
	14	6.5	—	17	2.5	—
	20	6.5	0.30	20	1.0	No suspension
Nitrogen	34	4.0	—			
	0	22.5	0.25	0	22.5	0.25
	3	17.0	—	3	11.5	—
	10	10.0	—	10	4.0	—
	14	8.5	—	14	2.5	—
	20	8.5	0.40	20	2.0	No suspension
	34	2.5	—	34	0	—

It was thought that loss of viscosity at high temperatures might be due to the initial moisture contents of the samples (about 10%). This was not evident in the present work as it required approximately two weeks to lower the moisture content of samples stored at 120° F. and 0% relative humidity to 2%. By that time a considerable amount of deterioration had already taken place. Accordingly, samples of commercial material were dried at 104°, 122°, and 140° F. under partial vacuum (25 in.). The materials were tested after 1, 2, 4, 6, 24, and 48 hr. of drying. The results in Table V show a marked decrease in viscosity as moisture was removed from the sample.

TABLE V

EFFECT OF DRYING TEMPERATURE ON VISCOSITY OF EXTRACTED GELOSE

Drying time, hr.	104° F.		122° F.		140° F.	
	Viscosity, MacMichael units	Moisture, %	Viscosity, MacMichael units	Moisture, %	Viscosity, MacMichael units	Moisture, %
Original material	80*	10.0	80	10.0	80	10.0
1	78	9.5	81	7.9	81	8.0
2	78	8.7	80	6.0	72	7.0
4	74	7.1	65	4.3	69	5.3
6	—	—	67	4.3	63	4.1
24	74	4.0	67	3.8	47	2.8
48	67	4.5	—	—	—	—

* All viscosity values were corrected for moisture content of sample.

When high temperature drying was found to be undesirable, a sample of dried extract was held for two weeks at 0° F. under partial vacuum (25 in.). The product then had 2% moisture and a viscosity equal to that of the original material. Portions of the original material and this dried product were then stored over phosphorus pentoxide at 120° F. The moisture content of both materials gradually decreased to zero and both decreased in viscosity. It appears, therefore, that deterioration at high temperatures is not due to the initial moisture content of the material.

Discussion

The present work shows that the suspending power and the viscosity of sols from Irish moss gelose prepared by different procedures are not related. Gelose finds its main use as a suspending agent in chocolate milk, and for this purpose the method of preparation does not appear to be important, since suspending power is a relatively stable property. For other uses (e.g., thickening agent in pharmaceuticals, cold water paints, etc.) where high viscosity is desired, the method of preparation may be extremely important, since viscosity is substantially affected by the method of preparation. High temperature drying appears to be particularly detrimental. The results indicate that products with high viscosity can be obtained by drying and concentrating by a freezing process, and that these extracts should preferably be stored at temperatures below 40° F.

While these experiments were not designed to determine the fundamental nature of the deterioration, it might be observed that, since the deterioration was more pronounced in samples of high moisture content and was associated with an increase in free sulphate, the changes resulting in a reduction of viscosity may be of a hydrolytic character.

Acknowledgments

The author wishes to thank Miss Edna Birchard for assistance in the experimental work, Dr. J. W. Hopkins for statistical advice, and the Krimko Co. for supplying samples of their product.

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PRODUCTION AND PROPERTIES OF 2,3-BUTANEDIOL

XXVI. VAPOR-LIQUID EQUILIBRIA OF THE SYSTEM *levo*-2,3-BUTANEDIOL - WATER¹

BY R. V. TOMKINS², J. A. WHEAT², AND D. W. STRANKS³

Abstract

A modified Othmer equilibrium still was used to obtain vapor-liquid equilibrium data for the *levo*-2,3-butanediol-water system at 14.7, 45, and 75 p.s.i. absolute. Comparison with similar data reported in the literature for the *meso*-2,3-butanediol-water system showed a greater volatility for the *levo*-isomer. There is an inflection in the equilibrium curves at lower diol concentrations.

Introduction

The design and operation of a pilot plant for the recovery of *levo*-2,3-butanediol from wheat mashes fermented by *Aerobacillus polymyxa* required information on the vapor-liquid equilibrium relations of the diol-water system. In particular, the equilibria data at elevated pressures were needed for evaluation of steam stripping of diol from concentrated mash. Knowlton, Schieltz, and Macmillan (3) have reported on this system at absolute pressures of 200, 400, 600 and 800 mm. of mercury. Blom *et al.* (1) have investigated the *meso*-2,3-butanediol-water system over a pressure range from 2.45 to 80 p.s.i. absolute, and Othmer and colleagues (8) from 200 to 760 mm. of mercury absolute. The present work with the *levo*-isomer includes data at 14.7, 45, and 75 p.s.i. absolute. The diol concentrations encountered in stripping operations are well within the range investigated.

Materials and Methods

levo-2,3-Butanediol

The butanediol used for this work was produced in the pilot plant of the National Research Laboratories by fermentation of wheat mash by *A. polymyxa*. The crude material was purified by two rectifications at 3 in. of mercury absolute, the first over sodium hydroxide to remove free and combined acids. The product was 97% diol, the remainder being water. The butanediol produced by this organism has been shown by Neish (5) to consist of the *levo*-isomer only.

Analytical Methods

Chemical analyses were used rather than physical measurements because of greater accuracy in the low diol concentration range. Solutions containing up to 90% diol were analyzed by the University of Wisconsin periodate method (4), the butanol extraction being omitted, as no interfering substances were present. The water content of solutions containing from 70 to 100% diol

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was determined with Karl Fischer reagent. In the range where both determinations were performed a mean value was obtained. The accuracy of both methods is about $\pm 0.5\%$. Hypodermic syringes were used as weight pipettes for handling the concentrated solutions, to prevent absorption of atmospheric moisture.

Apparatus

The equilibrium still used for this work was a modification of the glass Othmer still (6), constructed of brass pipe fittings to allow use at elevated pressures. A sketch including pertinent details and dimensions is shown in Fig. 1. The vapor jacket and vapor line to the condenser were insulated

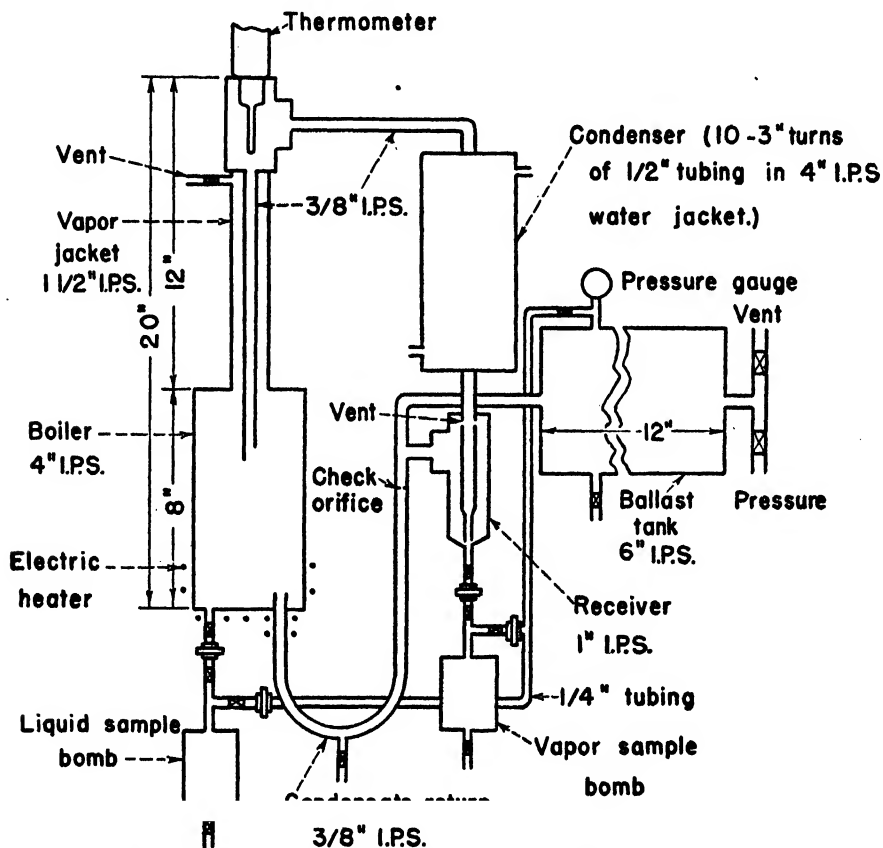


FIG. 1. Sketch of equilibrium still and auxiliary equipment, approximately to scale.

with about 2 in. of asbestos and 1 in. of 85% magnesia. The temperature of the vapors was measured with a Taylor industrial thermometer calibrated in 2°C . divisions and read to the nearest 0.5°C . This was used to aid in operating the still rather than to obtain boiling point data. The thermometer body was insulated with 1 in. of corrugated asbestos. The check orifice ($3/32$ in.) prevented surges in the return line. The voltage applied to an

external electric element¹ (32 ft. of 16 gauge Chromel wire) was controlled by a Variac transformer. Nitrogen was used for pressure operation, and the pressure was read on a calibrated Bourdon gauge.

Since this still was constructed, Othmer and Morley (7) have published a description of similar apparatus.

Operation

Certain precautions must be observed when operating the still to avoid false results. Refluxing must be prevented or the vapor sample will contain too much of the more volatile component. The insulation on the apparatus was sufficient to reduce condensation to a negligible value relative to the boiling rates used. Similarly incorrect values will be obtained if insufficient cycles occur in the condensate system because of too short a boiling period or too low a boiling rate. Low concentrations of the more volatile component in the vapor will be observed if entrainment results from too high a boiling rate.

The following experiment was undertaken to determine operating conditions at which these errors would be minimized. A series of distillations was carried on at atmospheric pressure, the boiling rate being varied. A charge of 850 ml. of approximately 20 weight % diol was used. In this apparatus, the liquid hold-up was larger than is common, and a five hour boiling period was used to assure that equilibrium would be established. The samples were analyzed and the vapor compositions calculated to a basis of 20.0 weight % diol in the liquid*. The results are presented graphically in Fig. 2.

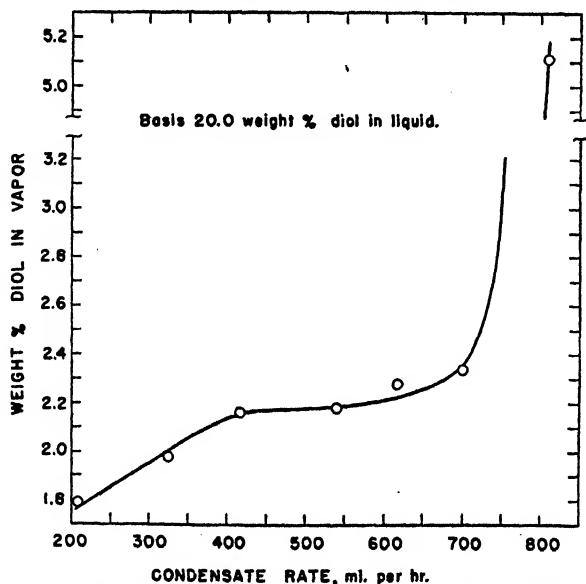


FIG. 2. Effect of boiling rate on apparent vapor composition.

* The calculations were made by considering the slope of the weight per cent diol in vapor vs. weight per cent diol in liquid curve to be 0.10 in the narrow range from 20.3 to 22.3 weight % diol into which the liquid samples fell.

Below 400 ml. per hr., equilibrium apparently had not been established. Between 400 and 550 ml. per hr. the vapor composition did not change significantly, and this is the range in which the still was subsequently operated. Above this rate, entrainment caused excessively high values for the diol concentration in the vapor. At higher pressures the same rate of boiling can be used, as the same number of cycles will occur in the condensate system, and the higher pressure reduces vapor velocity and hence entrainment. Excessively long boiling periods would have to be used for vacuum work, as the boiling rate has to be reduced greatly to prevent entrainment. Also, at very low boiling rates, there is danger of the small amount of reflux caused by heat loss having a significant effect on the distillation.

As the condensate receiver holds about 50 ml., the boiling rates selected result in 45 to 55 cycles during the five hour boiling period.

Samples were taken at superatmospheric pressure by means of bombs arranged, as shown in Fig. 1, so the pressure in the bomb was the same as that in the still. The liquid sample line was cooled when samples were taken to prevent flashing and consequent errors.

The heat input required at different pressure and concentration levels was determined by preliminary experiments, and the rate of boiling was checked at the end of each determination.

For a typical test, the 850 ml. of solution was charged to the still and brought to boiling with the vent open to allow fixed gases to escape. The system was then closed and nitrogen admitted slowly, so that boiling was not stopped, until the desired pressure was reached. The still was then left in operation for five hours. The valves from the bombs to still and condensate receiver were opened simultaneously, left open for about 30 sec., and then closed. All valves to the bombs were then closed; the bombs were removed and cooled; the pressure was released; and samples were removed and analyzed.

Experimental Results

The experimental data obtained are given in Table I, and presented on logarithmic scales (to spread the points at low diol concentrations) in Fig. 3. The conventional y - x diagram (Fig. 4) showing the equilibrium at atmospheric pressure also includes an enlarged portion at the three pressures investigated for diol concentrations below 20 mole %. It is obvious that there is an inflection at higher water concentrations, resulting in a reverse curve similar to that of the ethanol-water system, but very much farther removed from the $y=x$ line. The data are not correlated by the Van Laar equation (2) or the equations of White (10).

Fig. 5 relates vapor composition to absolute pressure at various liquid composition levels. The points fall on approximately straight lines up to 10 mole % diol in the liquid. Interpolation and extrapolation to lower

TABLE I

LIQUID AND VAPOR COMPOSITION OF *levo*-2,3-BUTANEDIOL SOLUTIONS

Pressure, p.s.i. absolute	Temperature, °C.	Weight % diol in		Mole % diol in	
		Liquid	Vapor	Liquid	Vapor
14.7	100	0.567	0.0608	0.114	0.0122
	100	2.18	0.291	0.444	0.0584
	100	5.30	0.734	1.105	0.1475
	100.5	11.00	1.30	2.40	0.263
	101	20.8	2.27	4.98	0.465
	101.5	38.5	3.67	11.11	0.753
	102.5	58.5	5.38	22.0	1.122
	105.5	74.3	8.47	36.7	1.815
	109	86.0	17.35	55.1	4.03
	114	88.1	19.9	59.6	4.74
	126	94.3	37.4	76.8	10.67
	138	96.8	55.2	85.6	19.8
	141	97.1	59.2	86.8	22.5
45	134.5	0.535	0.155	0.1075	0.0310
	134.5	1.373	0.352	0.278	0.0707
	134.5	5.70	1.328	1.192	0.268
	134.5	6.71	1.563	1.418	0.317
	135	14.0	3.30	3.15	0.676
	135.5	20.8	4.43	4.98	0.919
	136	39.0	6.90	11.32	0.460
	136.5	49.6	7.73	16.45	1.650
75	153	0.642	0.233	0.1290	0.0467
	153	1.946	0.682	0.395	0.137
	153.5	6.60	2.21	1.394	0.450
	154	14.55	3.59	3.29	0.739
	154.5	20.0	4.57	4.77	0.950
	155	37.0	7.09	10.50	1.500
	157.5	67.5	13.22	29.4	2.96

pressures appear justified, judging by the work of Blom *et al.* (1). Their results for the *meso*-diol are also shown on this figure for comparison. As would be expected from the difference in boiling points of the isomers the *levo*-shows greater volatility than the *meso*-, the difference being more pronounced at lower diol concentrations. The equilibria at atmospheric pressure are not in accord with the data of Knowlton *et al.* below 50 weight %. However as these workers used boiling point to determine composition, and the change of boiling point with composition is very small at low diol concentrations, it is believed that the present work using chemical analysis to determine composition is more reliable.

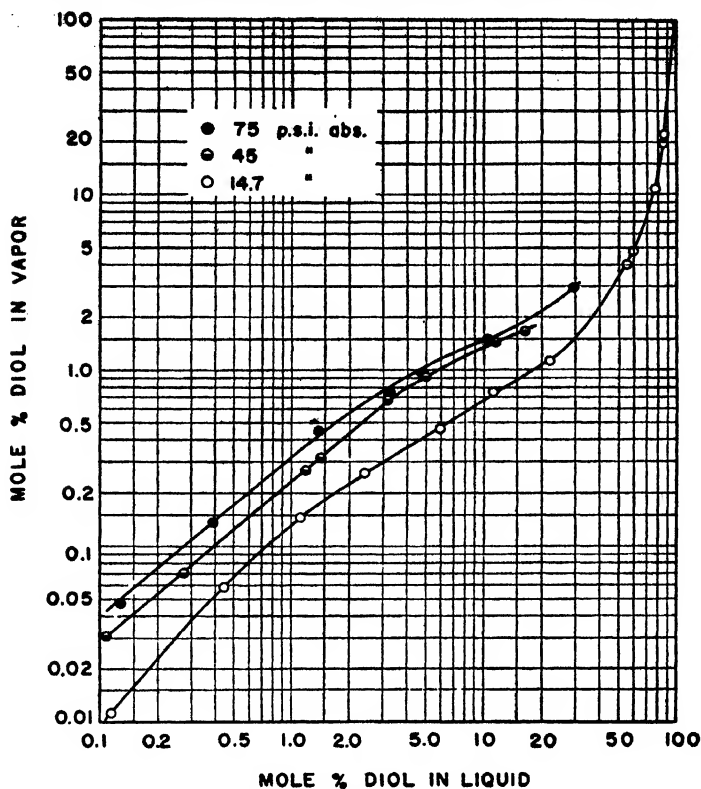


FIG. 3. Vapor-liquid equilibria for levo-2,3-butanediol, plotted on a logarithmic scale.

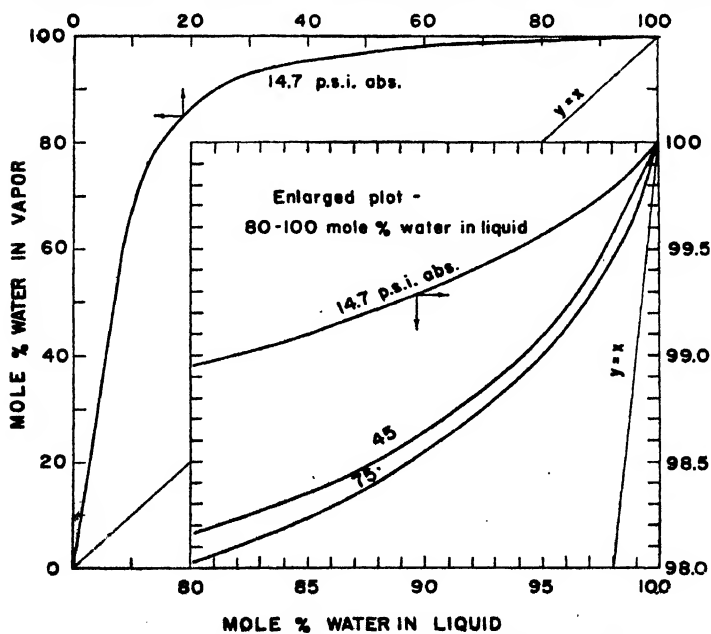


FIG. 4. Vapor-liquid equilibria of levo-2,3-butanediol.

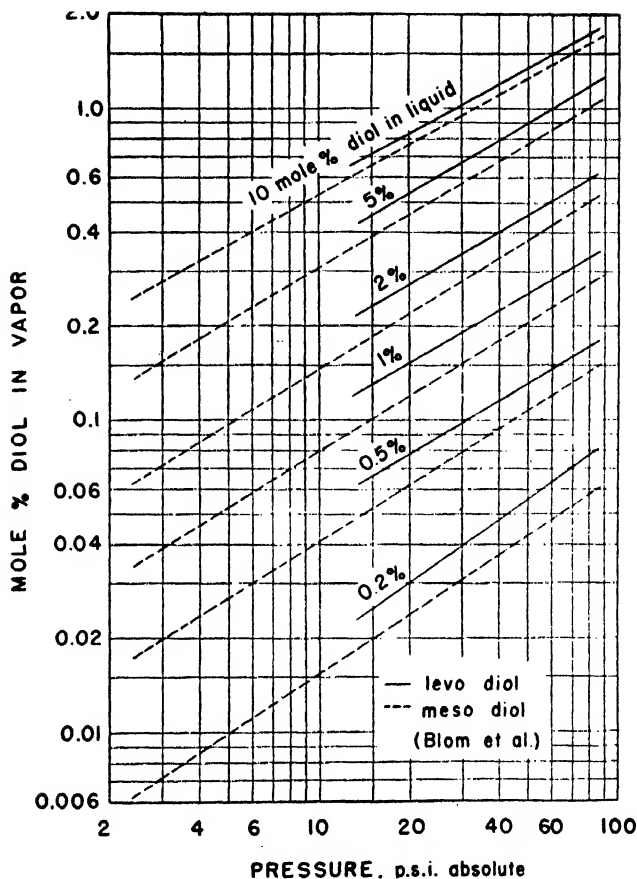


FIG. 5. Vapor-liquid equilibria of levo- and meso-2,3-butanediol (1), at various liquid compositions, showing effect of pressure on vapor composition.

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ANALYSIS OF STARCH SYRUP¹

By K. A. CLENDENNING², D. E. WRIGHT³, AND A. L. SHEWFELT⁴

Abstract

Examination of a number of starch syrups revealed wide differences in content of non-carbohydrates: water, 17.4 to 28.7%; protein 0.05 to 1.0%; ash 0.2 to 1.6%, sodium chloride 0.1 to 0.7% and sulphur dioxide 0 to 340 p.p.m. The commercial wheat syrups examined had high protein and salt contents, and a sample prepared by direct acid hydrolysis also contained an appreciable amount of ammonium chloride. Maximum absorption by storage color was observed at 3500 to 4500 Å; this region is therefore suitable for routine color measurements. Steinhoff's empirical copper acetate procedure for the direct determination of dextrose was found to be strongly influenced by heat treatment, total salt, and copper concentration; it was not improved by changing the composition of the reaction mixture. Moisture data obtained by vacuum oven and toluol distillation methods showed close agreement on syrups of widely different dextrose equivalent value; an improved stirring device is described for the incorporation of syrup and dispersing agent in either of these procedures.

Introduction

Preliminary to an investigation of starch syrup production (6), a study was made of analytical methods and of the composition of commercial products. Observations on factors influencing the analytical determinations and modifications that proved advantageous are described in this paper. Data also are presented on the composition of domestic and imported corn, wheat, and potato syrups that were marketed during the past four years.

Methods of Analysis

Sodium chloride contents of the ashed samples were estimated from sodium determinations with magnesium uranyl acetate (1). Sulphur dioxide was determined on diluted (1 : 1) 50 gm. syrup samples by adding alkali and titrating with iodine (11). Optical rotatory power was determined at 20° C. on 100 ml. solutions containing 26 gm. solids, and was expressed as 'specific rotation' on a total solids basis. Dextrose equivalent, also expressed on a solids basis, was determined by Zerban and Sattler's modification of the Shaffer-Hartmann method (25).

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Total Nitrogen

The digestion proceeded satisfactorily and quantitative nitrogen recoveries were obtained when 5.0 to 7.5 gm. syrup solids and 45 cc. sulphuric acid were employed in the Kjeldahl nitrogen determinations. These conditions are considered superior to those that have been prescribed previously (9, 22). The accuracy of the determination suffers from the use of 1 to 2 gm. samples (22), particularly when dealing with high quality syrups having total nitrogen contents of 10 to 20 mgm. %. With 10 gm. samples (9), the digestion mixture is very apt to solidify before clearing.

Ammonia Nitrogen

Folin's aeration method (10) proved fairly satisfactory when adapted as follows. Ten grams syrup solids was dissolved in 50 ml. water and transferred to a Kjeldahl flask. Ammonia-free air was drawn through the solution for one-half hour. Two grams of sodium carbonate was added and the solution was aerated at the rate of 30 liters per hour for five hours. During aeration, the liquid temperature was maintained between 35° and 40° C. The liberated ammonia was absorbed in *N*/140 sulphuric acid. Recoveries with 1 and 3 mgm. additions of ammonium chloride in the presence of 10 gm. starch syrup were 90 and 95% respectively.

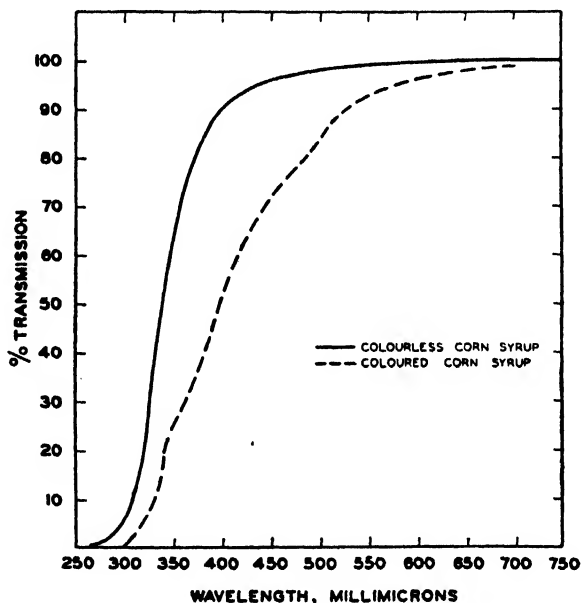


FIG. 1. Spectral transmittance of freshly prepared 42° Bé. corn syrup (50 D.E.) and of syrup that had developed color during storage.

Color

The transmission curves of Fig. 1 were determined with a Beckman spectrophotometer against distilled water blanks. Absorption was high at the blue and low at the red end of the visible spectrum with both the colored

and colorless syrups (unblended), and neither syrup showed definite absorption bands. Similar characteristics have been reported by Wayne (23) for cane molasses, caramel solutions, and raw cane sugar solutions. Since the largest difference in transmission between the colored and colorless starch syrups was shown between 350 and 450 $m\mu$, Filter 420 was selected for subsequent color measurements with the Evelyn colorimeter (6). A syrup of corresponding density that had been rendered colorless with activated carbon was used as a standard.

The Copper Acetate Procedure for Dextrose

The copper acetate procedure developed by Steinhoff (21), in which 50% sodium acetate solution replaces Fehling's II, has attracted interest as a convenient means of determining the actual dextrose content of starch syrups (19, 20, 25). Later modifications (20, 25) are chiefly concerned with the determination of the reduced copper rather than with the reaction itself. The procedure suffers from its relative insensitivity to dextrose contents of from 40 to 100 mgm. (Fig. 2) and agreement between duplicates is usually

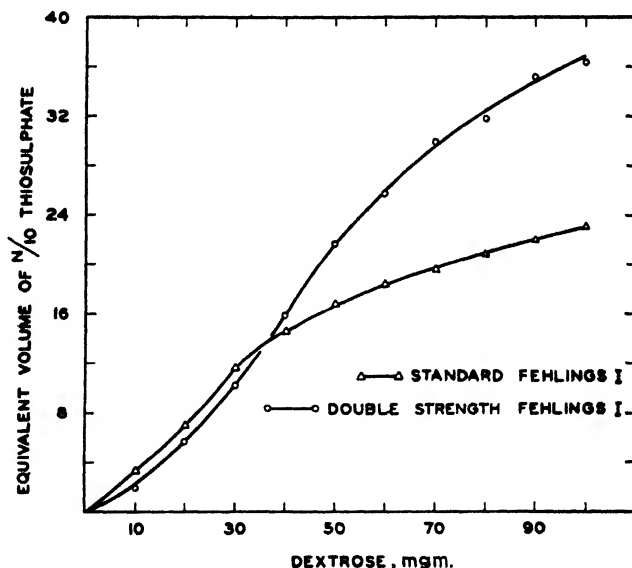


FIG. 2. Effect of increased copper content on the reduction of Steinhoff's copper acetate solution by 10 to 100 mgm. dextrose (30 min. at 100° C.).

poorer than is obtained in routine applications of copper tartrate procedures. The literature (19, 20, 21, 25) revealed a complete lack of information on the effects of heating time and composition of the reaction mixture on copper reduction by dextrose.

A plateau in copper reduction is not attained either after 20 min. or longer periods in the boiling water bath.

Time at 100° C., min.:	5	10	15	20	30	40	60
Equivalent volume of <i>N</i> /10 $\text{Na}_2\text{S}_2\text{O}_3$ for 50 mgm. dextrose, ml.	6.57	13.0	15.4	16.2	16.7	17.2	17.5

Differences in wall thickness between flasks, in bath temperature, and in agitation cannot be avoided entirely, and the resulting variations in heat treatment may be expected to influence the results.

When the usual 50 ml. volume is maintained, reduction of Steinhoff's copper acetate solution by dextrose is strongly depressed by the addition of either sulphuric acid or sodium hydroxide (Fig. 3). These observations signify that this procedure, in common with the ferricyanide and copper methods for reducing sugars examined by Weintraub and Price (24), is strongly influenced by initial pH and salt content.

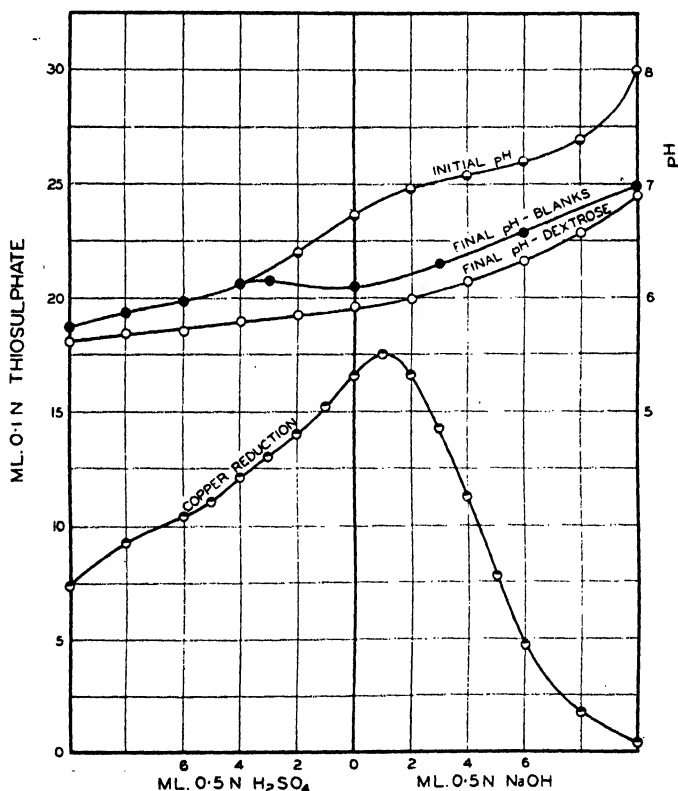


FIG. 3. Effect of alkali and acid additions on the reduction of Steinhoff's copper acetate solution by 50 mgm. dextrose (30 min. at 100° C.).

It has been claimed (20, 21) that no change in pH occurs during reduction of the copper acetate reagent, since free acetic acid is not present as in the older Barfoed reagent. Fig. 3 shows that an appreciable decrease occurs, and that the pH change is greater in the presence than in the absence of dextrose.

Doubling the copper content of the reaction mixture effects drastic changes (Fig. 2). With 40 to 100 mgm. dextrose, copper reduction was increased by as much as 50%, but copper reduction was slightly diminished at lower dextrose contents. The data were more erratic at high dextrose concentrations when double strength Fehling's I was employed, irrespective of the acetate level. Interference by maltose was also increased. For example, copper reduction by 50 mgm. maltose in the presence of 50 mgm. dextrose was increased from the equivalent of 0.74 ml. *N*/10 sodium thiosulphate at the usual copper concentration to 1.64 ml. when the copper concentration was doubled.

Considerable exploratory work indicated that the copper acetate procedure is not improved by changing the composition of Steinhoff's reaction mixture. Corrections were not made for the slight reducing action of maltose in routine applications because of existing uncertainty respecting the magnitude of its effect and the present lack of agreement concerning the actual maltose content of typical starch syrups (12, pp. 269-270; 18). Some improvement in reproducibility was indicated with 30-min. heating periods, but the procedure otherwise was applied in accordance with earlier directions (25).

Moisture

With proper precautions, the water content of starch syrup may be approximated with a hydrometer spindle (7, 8) or refractometer (5, 13) but the extremely high viscosity of syrup is a troublesome feature in both methods. The density and refractivity of starch syrups also are considerably influenced by degree of hydrolysis and salt content.

The chief obstacles in direct determinations of water content are the vitreous state that is attained before water is completely removed, high initial viscosity which impedes uniform distribution on dispersing agents, and the uncertain effects of impurities on sugar decomposition. The direct methods that have been proposed differ chiefly in the means provided for sample dispersion. Drying on quartz sand, pumice, and coiled filter paper was tested, but in our experience was less satisfactory than oven and distillation methods in which Filter-cel is employed.

The distillation method prescribed for '70' and '80' corn sugar by Cleland and Fetzer (4) was employed with minor changes. Toluol was substituted for benzene. A correction of 0.04 ml. per 100 ml. toluol was applied for water solubility. Anhydrous Hyflo Supercel was employed as the dispersing agent. The syrup, dispersant, and toluol were worked to a uniform mass with the stirring device shown in Fig. 4. The handle of the stirrer was then detached, leaving the pestle in the distillation flask. The stirring device (Fig. 4) is made from 12/30 S/T joints, and in our experience has been more satisfactory than any device that has previously been prescribed for this purpose.

After the distillation apparatus was assembled, the flasks were placed in a Stanolax* oil bath having an initial temperature of 137° C. The bath temperature was adjusted to 132° to 133° C. as boiling began, and was subsequently maintained at this temperature. The moisture traps were immersed in a 20° C. bath for one hour before volume readings were taken. (Frozen



FIG. 4. Improved stirrer for use in the determination of moisture in syrups.

joints were freed by tapping with a graphite block.) Additional precautions with respect to the care of the distillation equipment were observed as recommended elsewhere (17).

It was found that appreciable water was recovered after a six hour distillation, and that distillation was complete in 12 to 16 hr.

Sample	Distillation time with toluol, hr.				
	4.5	6.5	12	16	22
	Apparent moisture content, %				
I	18.45	18.82	19.05	19.10	19.10
	18.81	19.03	19.21	19.21	19.21
II	19.11	19.22	19.38	19.38	19.38
	18.85	18.97	19.32	19.32	19.32

The higher boiling point of toluol did not reduce the distillation time for syrup appreciably below that required in distilling moisture from corn sugars with benzene (4). Less time apparently is required for the complete removal of water from starch syrups by toluol distillation than from 10 mesh and 40 mesh corn meal (15, 16).

* Stanolax was found superior to glycerol or corn oil as bath liquid for the distillations. After the first day's use, smoking was negligible and there was no formation of tarry deposits.

The Filter-cel vacuum oven method for starch syrup described by Cleland and Fetzer (3) was adopted for routine applications with minor changes, employing a drying period of 20 to 24 hr. (See "Adaptation of Filter-cel method" (3, p. 859.)) The stirring device described above was used in mixing the diluted syrup with the Filter-cel. The diluted samples were dried for two and one-half to three hours in a 100° C. air oven before transferring to the 100° C. vacuum oven. The vacuum oven was operated at approximately 15 mm. mercury and was equipped with the drying train prescribed by Sair and Fetzer (15).

The apparent moisture contents reported in the accompanying table were observed by vacuum oven drying of a syrup that showed 21.0% moisture by a 20 hr. distillation with toluol.

Moisture dish size, in.	Drying time <i>in vacuo</i> at 100° C., hr.							
	4	8	12	16	20	24	28	32
2½ by ½	Apparent moisture content, %							
	20.33 20.01	20.68 20.68	20.73 20.75	20.83 20.83	20.85 20.85	20.85 20.85	20.89 20.90	20.93 20.94
3½ by 2		20.84 20.98	20.89 20.96	20.91 20.96	20.98 21.01	20.98 21.03	20.99 21.03	21.02 21.06

Extension of the drying period from 16 to 32 hr. resulted in a very gradual loss in weight, averaging less than 0.01% per hour. The values obtained by drying periods of 16 to 32 hr. *in vacuo* agreed with the 20 hr. toluol distillation value within 0.15%. A small but consistent difference in apparent moisture content was associated with the size of the drying dishes. This result may have been fortuitous, but it at least indicates that drying is more rapid and complete from the shallow syrup-Filter-cel masses of the larger dishes. The larger dish size also was more convenient and was therefore adopted for routine use.

Agreement between the toluol distillation and vacuum oven methods was not affected by degree of conversion between 30 and 70 D.E. The largest differences between duplicates were observed with the distillation method on extremely viscous syrups containing less than 18% water. In routine applications, agreement between duplicates usually was within 0.05% by the oven method and 0.2% by toluol distillation.

Composition of Commercial Starch Syrups

The syrups of Table I were obtained from commercial sources. The table corn syrups were of the usual golden type prepared by blending refiners' syrup (sucrose) and starch syrup. Medium conversion corn syrup ('C.S.U.', 'confectioners' glucose') differs from these only in that it lacks added sucrose and coloring. The Argentine and Mexican syrups were imported for sale in Canada as sugar substitutes. The wheat and potato syrup samples represent

TABLE I
COMPOSITION OF COMMERCIAL STARCH SYRUPS

Sample	Water, %	Protein N \times 6.25, %	Ash, %	Sodium chloride, %	pH	SO ₂ , p.p.m.	$[\alpha]_D^{20}$ (solids)	Dextrose, %	Dextrose equi- valent, % of solids
Table corn syrup	24.7	0.05	0.35	0.18	4.63	<10	142	16.2	40.8
Table corn syrup	24.1	0.12	0.24	0.11	5.51	<10	138	18.7	41.3
Corn syrup, medium conversion unmixed	19.5	0.12	0.21	0.20	5.32	290	151	17.5	40.8
Corn syrup, low con- version	18.7	0.11	0.19	0.18	5.20	<10	165	6.3	27.3
Hydrol	24.0	0.33	4.77	—	4.00	<10	—	43.5	69.3
Argentine corn syrup	20.1	0.22	0.36	0.24	4.79	<10	151	18.7	38.5
Mexican corn syrup	17.4	0.10	0.35	0.24	5.08	340	154	15.4	36.2
Potato syrup	18.5	0.07	0.28	0.23	4.30	<10	141	22.5	39.4
		(N \times 5.7)							
Wheat syrup No. 1	18.6	0.10	0.25	0.22	4.58	<10	126	27.7	53.7
Wheat syrup No. 2	23.3	1.01	0.64	0.46	5.22	<10	127	22.4	51.4
Wheat syrup No. 3	23.9	0.50	0.81	0.63	4.98	<10	126	26.0	51.1
Wheat syrup No. 4	27.2	0.83	1.58	0.64	4.95	<10	—	14.6	37.0
Wheat syrup No. 5	28.7	0.65	1.51	0.68	5.00	<10	—	23.3	41.5
Wheat syrup No. 6	20.7	0.68	1.25	0.38	5.15	<10	145	23.4	39.4

wartime products that were produced in Canada to the extent of 500 to 1000 tons per month.

The water contents ranged from 17.4 to 28.7%. Samples containing over 25% water fermented during subsequent storage, whereas those containing less than 19% water were extremely viscous and difficult to handle.

The protein content of the corn and potato syrups was approximately 0.1%, whereas that of the commercial wheat syrups usually was between 0.5 and 1.0%. The low protein content shown by wheat syrup No. 1 indicates that the starch employed in its preparation was of high quality. This sample was very similar in taste and appearance to the potato and medium conversion corn syrup samples. The syrups of higher nitrogen content usually had considerable off-taste, were strongly colored, and developed turbidity and flocculent precipitates after lengthy storage periods.

According to Parow (14), potato syrup is superior to corn syrup for making confectionery because of its lower nitrogen content and correspondingly diminished tendency to develop color in the candy kettle. Some support for this is provided by the fact that commercial corn starch usually contains a higher content of nitrogeneous impurities than potato starch. The corn syrups employed by Parow in his comparisons, however, were prepared from corn starches of exceptionally high protein content (0.5% and higher). Similar heating tests applied to the present commercial products indicated lesser discoloration by the corn and potato syrups than by the wheat syrups. No difference in color development was detected between the corn and potato

syrups, however, and the same result was obtained with corn and potato syrups prepared in the laboratory.

The total ash and sodium chloride values of Table I indicate large variations in content of extraneous inorganic matter. Impurities introduced with the process water or by corrosion have deleterious effects such as storage haze (6), promotion of discoloration (6), and production of an astringent taste (2, p. 130). Most of the wheat syrups contained sufficient sodium chloride to impart a perceptibly salty taste. The high sodium chloride content of 'Hydrol' is a result of the large amount of hydrochloric acid employed in dextrose production (up to 1% hydrochloric acid on the dry weight of starch) and of the concentration of salt in the mother liquor that accompanies dextrose crystallization.

The pH of all syrups was approximately 5.0, which apparently was the neutralization level used in their production. The sulphur dioxide content of starch syrups is not subject to statutory regulation in Canada, and in two instances exceeded 250 p.p.m.

The dextrose equivalent or 'purity', true dextrose, and specific rotation values reflect different aspects of starch hydrolysis, but under standard conditions of manufacture any one of these could be used to designate degree of conversion. 'Medium purity' corn syrups showed specific rotation values of approximately 150, true dextrose contents of approximately 18%, wet basis, and dextrose equivalent values of 40 or slightly higher. The 'low purity' or brewers' body syrup had a specific rotation above 160, true dextrose contents of less than 10%, and dextrose equivalent values of 25 to 32. The high content of complex dextrans in the latter syrup rendered it densely opaque. The degree of conversion shown by the sample of Mexican corn syrup (36 D.E.) represents the borderline between 'body' and 'regular' syrups. Hydrolysis in this instance had proceeded just far enough to prevent the development of opacity. Most of the wheat syrups showed specific rotation values of 125 to 130, dextrose contents of approximately 25%, and dextrose equivalent values of 50 or higher. As these products were intended for use as sweeteners, their hydrolysis was often allowed to proceed further than in the production of 'medium' purity corn syrup.

Ammonium Chloride in Starch Syrups

Amide groups of the protein impurities in the raw starch could be liberated by hydrolysis and appear in finished syrup as ammonium chloride. Laboratory experiments provided support for this supposition and indicated that high concentrations of acid, as were being used in wheat syrup production, stimulated the production of ammonium chloride. It was also observed that addition of as little as 25 mgm. % ammonium chloride conferred a definite 'off-taste' to table corn syrups, and that 7 mgm. % ammonium chloride was detectable in tap water.

Folin's adapted method (10) gave the following ammonia values, expressed as ammonium chloride, for commercial starch syrups: table corn syrup,

9 mgm. %; unmixed corn syrup, 11.6 mgm. %; wheat syrup No. 1, 11.6 mgm. %; wheat syrup No. 2, 18.1 mgm. %; and wheat syrup No. 4, 222 mgm. %. Among these syrups, only the last, which was prepared by the acid hydrolysis of wheat flour, was found to contain sufficient ammonium chloride to exceed the concentration at which its objectionable taste is perceptible.

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POLARIMETRIC DETERMINATION OF STARCH IN CEREAL PRODUCTS

V. THE PARTICLE SIZE AND EXTRACTION TIME REQUIREMENTS¹

BY K. A. CLENDENNING²

Abstract

Grinding wheat to pass a 40 mesh screen is adequate for polarimetric starch analyses. Finer grinding does not influence the precision, apparent starch content, or extraction time requirement appreciably. The pentosan content of calcium chloride extracts is increased by fine grinding and by prolonged extraction and is decreased by preliminary extraction with dilute alkali. The wheat products employed in this study were subjected to complete analysis by conventional methods (ash, fat, protein, sugar, pentosan, polyuronide, fiber). Starch contents calculated by difference were in close agreement with direct determinations on patent flour, and showed differences of 1.3 to 2.6% on whole wheat. Apparent fat contents, determined with ethyl ether or petroleum ether, were doubled by preliminary acid digestion. Wheat is shown to have an appreciable polyuronide content, which is located in the integuments.

Introduction

Preparatory grinding to an impalpable flour has been prescribed almost invariably in polarimetric procedures for starch in cereal grains (9, 11, 12, 16, 17). The directions of Ewers (11) and Hopkins (12) specify samples that pass 125 and 100 mesh screens, respectively. This requirement is usually time-consuming in routine analyses, and except for wheat gluten (4), is not supported by published data. Earle and Milner (8) recommend grinding to pass the 0.5 mm. Wiley screen in the analysis of wheat and corn. Lampitt *et al.* (15) have shown that lengthy ball-milling greatly increases the solubility of starch in cold water. If the samples are extracted with cold water or dilute alkali prior to starch dispersion and polarization (8), starch losses then become possible as a result of thorough grinding.

The present paper provides information on the particle size and extraction time requirements in calcium chloride polarimetric procedures for starch in whole wheat and wheat flour. The samples were subjected to complete analysis by conventional methods to provide approximate values for starch by difference. Experiments also are reported on the effects of sample size on starch recovery, and of particle size and extraction time on pentosan solubilization.

Materials and Methods

Hard Red Spring wheat samples were ground in a Wiley mill equipped with bottom screens having 1 mm. and 2 mm. circular openings. Subsamples were

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ball-milled, and the accompanying increase in ash content (0.1 to 0.3%) was allowed for in the calculations. The wide range of particle sizes represented by the samples used in this study is shown in Table I.

TABLE I
SIEVE ANALYSES OF WHOLE WHEAT AND GRANULAR FLOURS, %

Screen mesh	Whole wheat 1			Whole wheat 2		Granular flour	
	Wiley-milled, 2 mm. screen	Wiley-milled, 1 mm. screen	Ball- milled	Wiley-milled, 1 mm. screen	Ball- milled	As received	Ball- milled
Retained on 20	36.3	Nil	Nil	Nil	Nil	Nil	Nil
Retained on 40	47.6	51.7	1.4	69.7	1.6	26.3	Nil
Retained on 60	5.8	23.6	5.2	12.9	6.6	35.8	Nil
Retained on 80	2.1	4.8	4.2	3.7	3.9	13.1	0.1
Retained on 100	1.9	1.9	1.1	2.1	2.3	11.1	0.3
Passed 100	6.3	16.0	88.1	11.6	85.6	13.7	99.6

Ash and crude fiber contents were determined by the conventional A.O.A.C. methods (2). In calculating protein contents from Kjeldahl nitrogen values, a factor of 5.7 was used for wheat flours and of 5.83 for whole wheat as recommended by Jones (14). Total sugar was estimated by the A.A.C.C. ferri-cyanide method (1). Moisture was determined by drying *in vacuo* at 100° C. for 20 to 30 hr. Values obtained by this method on starches, flour, and whole wheat agreed within 0.1% with those obtained by 60 hr. distillation with toluol under the conditions prescribed by Sair and Fetzer (18). The A.O.A.C. acid hydrolysis-ether extraction method (2, p. 240), which was selected for the determination of crude fat contents, gave values approximately twice as high as those observed with 24-hr. ethyl ether and petroleum ether extraction treatments of various wheat fractions (Table II).

TABLE II
A COMPARISON OF METHODS FOR THE DETERMINATION OF CRUDE FAT IN WHEAT PRODUCTS, %

	Ethyl ether*	Petroleum ether*	Acid hydrolysis -ether
Wheat starch	0.28	Nil	0.48
Wheat flour	0.71	0.75	1.60
Whole wheat flour	2.08	1.80	3.00
Gluten (100 mesh)	0.63	0.43	5.00

* By 24-hr. Soxhlet extraction.

In determining pentosan contents, 5-gm. samples were distilled with 12% hydrochloric acid at the usual rate of 3 ml. per min. until a negative test for furfural was obtained with aniline acetate. The distillates were redistilled at the same rate in the presence of 20% sodium chloride (19). A correction

of 3% was applied for furfural destruction in the second distillation. Furfural was determined at 0° C. by the Hughes-Acree method (13). In accordance with Krober's formula (2, p. 413), the yield of furfural in the first distillation was assumed to be 83% of the theoretical, or 58.5% of the pentosan content.

Polyuronide content was estimated by decarboxylation of 5- to 10-gm. samples in accordance with the directions of Dickson *et al.* (7). The Truog absorption tower assembly was constructed entirely of glass, 34/45 ST joints being substituted for the troublesome rubber connections on the column. Campbell *et al.* (3) have recommended the use of an aniline trap as a means of excluding furfural from the absorption tower. Tests with freshly distilled furfural showed it to have a slight neutralizing action on barium hydroxide, 1 gm. of furfural being equivalent to 1.94 ml. *N*/10 hydrochloric acid or 4.3 mgm. carbon dioxide. As the samples with which we were concerned produced 200 mgm. or less of furfural, its exclusion (3) appeared to be an unnecessary refinement. In agreement with Whistler *et al.* (20), production of 2.64 mgm. carbon dioxide per gram of pure glucose, or per gram of starch expressed as glucose, was observed with the usual five hour refluxing period. A correction based on the measured starch and sugar contents of the samples was accordingly made for this source of carbon dioxide in the polyuronide determinations. The corresponding yield of carbon dioxide from gliadin and gluten samples was 0.85 mgm. carbon dioxide per gram, for which corrections were not introduced.

In testing the effects of particle size on starch recovery and reproducibility, the extraction was conducted under the usual conditions (6) for periods of 15, 30, and 45 min. Judging from previous observations on pure starches (5), the effects of lengthened extraction treatments on the specific rotation of starch may be neglected. Protein precipitation and filtration were conducted as previously directed (6). All filtrations were rapid and the filtrates without exception permitted accurate polarimetric observations on 2-dm. tubes.

Results

Marked improvement in starch recovery and reproducibility (Table III) as a result of further grinding or prolonged extraction was observed only on the coarsest sample (Whole Wheat 1, 2 mm.). It should be noted that 36% of this sample would not pass a 20 mesh screen (Table I). Starch recovery from all samples ground in the Wiley mill to pass either a 1 mm. or 40 mesh screen was not increased by ball-milling to pass a 100 mesh screen or by extending the extraction to 30 or 45 min. (Table III). Since more than 50% of the 1 mm. samples would not pass a 40 mesh screen, grinding to the latter mesh size is adequate by a considerable margin. Agreement between duplicates on all but the coarsest sample was within 0.3% starch. The apparent starch content of the 40 mesh samples also was not changed (within 0.3%) by reducing the sample size from 2.5 to 1.5 or 0.5 gm.

Corresponding studies of the wheat gluten particle size requirement (4) indicated the necessity of extending the extraction to 40 min. for maximum

TABLE III

EFFECTS OF PARTICLE SIZE AND EXTRACTION TIME ON STARCH RECOVERY FROM WHOLE WHEAT AND GRANULAR FLOURS

Sample	Apparent starch content,* %		
	Extracted 15 min.	Extracted 30 min.	Extracted 45 min.
Whole Wheat I, 2 mm. screen	57.84	60.42	60.42
	59.09	60.30	60.52
Whole Wheat I, 1 mm. screen	62.09	62.42	62.09
	62.32	62.32	62.32
Whole Wheat I, 40 mesh	62.16	61.93	61.60
	62.26	62.04	61.60
Whole Wheat I, ball-milled	61.66	61.46	61.34
	61.66	61.46	61.46
Whole Wheat II, 1 mm. screen	58.74	58.64	58.17
	58.74	58.74	58.17
Whole Wheat II, 40 mesh	59.03	59.03	58.60
	58.93	58.82	58.47
Whole Wheat II, ball-milled	58.81	58.81	58.04
	58.93	58.70	58.04
Granular flour as received	76.82	76.82	76.82
	77.14	76.82	76.82
Granular flour ball-milled	76.84	76.41	76.18
	76.84	76.61	76.28

* Data are expressed on a basis of total solids, corrected for ash increments in milling.

starch recovery from 140 mesh samples. Evidently the wet separation of gluten and subsequent drum-drying treatments render it highly impervious to the starch solvent. Meeting the particle size requirement in this instance is simplified by the uniformity in composition of the different-sized gluten particles after coarse grinding. Analysis of the 'flour' fraction obtained by sieving Wiley-milled gluten samples in our experience has given the same result as when the entire sample is ball-milled to the required particle size.

It has been shown (6) that solubilization of bran hemicelluloses by boiling calcium chloride solution is promoted by high extraction temperatures and salt concentrations. The data of Table IV indicate that solubilization of wheat pentosans [*levo*-rotatory (6)] is also increased by reduced particle size and prolonged extraction. These differences are not sufficiently large, however, to influence polarimetric starch data. Similar experiments indicated that the pentosan content of the calcium chloride filtrate is reduced by 25% when 40 mesh whole wheat is subjected to preliminary extraction with dilute alkali as recommended by Earle and Milner (8).

Eva and Rankin (10) have previously provided extensive comparative data for starch analyses of whole wheat by five direct methods. Table V provides

data for polarimetric starch determinations by two methods, and for starch 'by difference' based on conventional methods for nonstarch constituents. The latter values should be regarded as approximations because of the doubtful accuracy of the methods employed in their calculation. Close agreement

TABLE IV
EFFECTS OF PARTICLE SIZE AND EXTRACTION TIME ON
PENTOSAN SOLUBILIZATION
(Milligrams pentosan dissolved per gram wheat solids)

Extraction time, min.	40 mesh	100 mesh
15	22.7	25.4
45	30.2	30.9

TABLE V
COMPOSITION OF WHEAT FLOURS, PER CENT, SOLIDS BASIS

	Whole Wheat I	Whole Wheat II	Granular flour	Patent flour
Ash	1.92	1.87	0.76	0.48
Fat (by acid hydrolysis)	3.82	4.42	1.45	1.58
Protein	15.09	19.52	13.27	15.04
Total sugar	4.10	4.00	2.34	2.18
Pentosan	6.64	7.25	2.91	1.93
Polyuronide	0.78	0.86	Trace	Trace
Crude fiber	2.63	2.78	0.71	0.18
Starch by difference	64.82	60.30	78.56	78.61
Polarimetric starch (alcohol extraction)	62.16	59.00	77.25	78.5
Polarimetric starch (stannic chloride precipitation)	62.20	58.96	76.84	78.2

is shown between the starch 'by difference' and 'by analysis' data for patent flour. Discrepancies of 1.3 to 2.6% are shown by the whole wheat data, and of 1.25 to 1.7% by the granular flour analyses.

Polyuronide determinations on wheat starch, patent flour, and gluten, corrected for carbon dioxide production by glucose and pure gliadin in terms of total carbohydrate and protein, indicated negligible contents of uronic acid residues. Corresponding analyses of whole wheat and 100 mesh wheat bran indicated contents of 0.8 and 3.9% respectively. In contrast to pentosans, which are found in all parts of the wheat kernel, the polyuronide fractions apparently are restricted to the integuments.

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THIAMINE AND RIBOFLAVIN CONTENT OF WHEAT, BARLEY, AND OATS GROWN IN DIFFERENT SOIL ZONES IN ALBERTA¹

L. W. McELROY,² J. KASTELIC,³ AND A. G. MCCALLA⁴

Abstract

A study was made of the thiamine and riboflavin content of Marquis wheat, Newal barley, and Victory oats grown in Alberta in the years 1944 and 1945 under widely different conditions of soil and climate. The mean thiamine content of Victory oats, 5.6 ± 1.5 μ gm. per gm., was found to be significantly higher than that of Marquis wheat, 4.4 ± 1.2 , or of Newal barley, 4.6 ± 1.0 μ gm. per gm. A positive correlation between protein and thiamine content was demonstrated in wheat and oats but not in barley. In all three grains the mean thiamine content of samples grown in the brown soil zone was significantly higher than that of samples grown in the gray soil zone. The mean values obtained for riboflavin were 1.34 ± 0.23 , 1.25 ± 0.25 , and 1.27 ± 0.18 μ gm. per gm. in wheat, barley, and oats, respectively. No significant correlation between protein and riboflavin was found in any of the three cereals. The mean riboflavin content of samples of wheat, barley, and oats grown on gray soils was slightly lower than that of samples grown on black or brown soils.

Introduction

Owing to the fact that a relatively high proportion of the calorie intake of both humans and farm livestock is made up of cereal grains or their products, the questions of vitamin levels and factors which may influence these levels in grains are of considerable interest. The results of several investigations (3, 5, 8, 9, 10, 16) indicate that, in wheat, thiamine levels may be related to a number of variables including type and variety, protein and ash content, kernel and bushel weight, and the environment in which the grain is grown. The factors which may influence or be related to thiamine levels have been less thoroughly studied in barley and oats than in wheat.

Data regarding the riboflavin content of Canadian grains are meager. The results of studies conducted in the United States (2, 3) show that the riboflavin content of cereal grains is lower and less variable than is the thiamine content, and suggest that such factors as environment, variety, and protein content may be less important in relation to riboflavin than to thiamine accumulation.

The objectives of the present investigation were:

(1) To obtain data on the relative thiamine and riboflavin content of wheat, barley, and oats grown in Alberta.

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(2) To study the correlation between protein and vitamin content in each of these cereal grains.

(3) To determine whether vitamin content could be related to the type of soil on which the grains were grown and whether such relation between thiamine or riboflavin content and soil is the same in all three grains.

Experimental

Assay Material

The grains studied were Marquis wheat, Newal barley, and Victory oats grown in the years 1944 and 1945. Samples were chosen to cover a wide

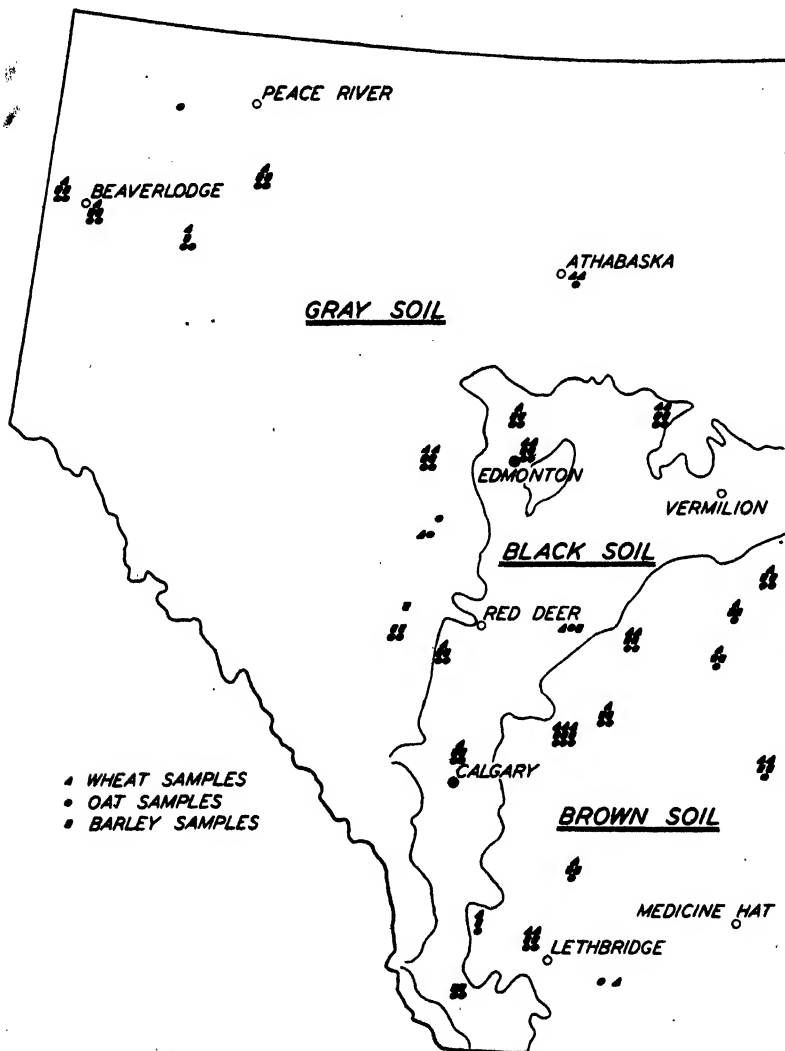


FIG. 1. Locations in which samples were grown.

range in protein content and to represent grains grown under a variety of soil and climatic conditions. They were obtained from University of Alberta test plots and from Dominion Illustration and Experimental Stations located in representative soil zones throughout the province of Alberta. The locations from which grain samples were secured, together with an outline of the major soil zones in Alberta, are given in Fig. 1. Additional information regarding the location, climate, and fertility of the soil zones of the province is given in "Soil Zones of Alberta" (14). An attempt was made to obtain an equal number of samples of each grain from each location, but as is evident from the distribution map (Fig. 1) this was not possible in all cases. It should also be noted that in Fig. 1 and in the text, gray and gray transition zones are grouped as 'gray,' black and shallow black as 'black,' and brown and dark brown as 'brown' soil zones.

Assay Methods

Protein.—Nitrogen was determined using the Kjeldahl method with mercuric oxide as catalyst. Protein in wheat is reported as nitrogen $\times 5.7$ and in oats and barley as nitrogen $\times 6.25$. All protein and vitamin assay results are expressed on the basis of 13.5% moisture.

Thiamine.—Thiamine assays were conducted on finely ground samples of grain by the yeast fermentation method of Schultz, Atkin, and Frey (12). Representative values obtained by this method as compared to those obtained by a modification of the Hennessy (6) thiochrome method are given in Table I. The values shown are averages of the results of a minimum of four assays done in duplicate. Although some variation is apparent in the thiamine values of individual samples as determined by the two methods, the means for wheat and barley do not suggest that there is any significant difference

TABLE I
FERMENTATION AND THIOCHROME THIAMINE ASSAY VALUES FOR CEREAL GRAINS

Grain	Sample	Protein, %	Fermentation, $\mu\text{gm.}/\text{gm.}$	Thiochrome, $\mu\text{gm.}/\text{gm.}$
Wheat	1	19.7	6.4	5.6
	2	13.7	4.9	4.6
	3	9.2	3.6	4.1
			Mean 5.0	4.7
Barley	1	17.1	7.4	7.6
	2	13.0	4.3	4.0
	3	9.4	4.1	4.3
			Mean 5.3	5.3
Oats	1	16.3	7.6	8.4
	2	12.3	5.4	6.2
	3	9.6	4.2	5.0
			Mean 5.7	6.5

between fermentation and thiochrome assay values for these two cereals. Thiamine levels in oats, as measured by the thiochrome method, were about 15% higher than those obtained by the fermentation method.

Riboflavin.—Riboflavin assays were done by a modification of the method of Snell and Strong (13) using *Lactobacillus casei-e* as the test organism. Samples were prepared by autoclaving in 0.1 *N* hydrochloric acid for 20 min. at 15 lb. pressure, followed by adjustment to pH 4.5, filtration, and extraction with ether as recommended by Strong and Carpenter (15). It was found necessary to add 1 ml. of a saturated solution of dibasic potassium phosphate to the extracts after ether treatment in order to precipitate excess calcium. After incubation for 72 hr., the contents of the assay tubes were rinsed into 100 ml. beakers and titrated with 0.1 *N* sodium hydroxide to pH 6.8, as measured by a potentiometer fitted with outside electrodes. As is shown in Table II, results obtained by this method were in good agreement with those obtained by the fluorometric method described by Andrews (1).

TABLE II
COMPARISON OF MICROBIOLOGICAL AND FLUOROMETRIC RIBOFLAVIN ASSAY
RESULTS FOR WHEAT, BARLEY, AND OATS

Grain	Sample	Protein, %	Method	
			Microbiological, $\mu\text{gm.}/\text{gm.}$	Fluorometric, $\mu\text{gm.}/\text{gm.}$
Wheat	1	19.7	1.32	1.25
	2	13.7	1.22	1.16
	3	9.2	1.20	1.05
			Mean	1.15
Barley	1	17.1	1.23	1.24
	2	13.0	1.50	1.33
	3	9.4	1.28	1.23
			Mean	1.27
Oats	1	16.3	1.54	1.58
	2	12.3	1.23	1.28
	3	9.6	1.36	1.26
			Mean	1.37

Results

A total of 31 samples of Marquis wheat, 43 of Newal barley, and 50 of Victory oats were assayed for thiamine. A few additional samples were assayed for riboflavin so that the totals for numbers of samples assayed for this vitamin are 37, 47, and 50 for wheat, barley, and oats, respectively. The results are summarized in Table III.

The mean of 4.4 $\mu\text{gm.}$ per gm. for the thiamine content of Marquis wheat is in good agreement with the value of 4.3 $\mu\text{gm.}$ per gm. (653 I.U. per lb.)

TABLE III

THIAMINE AND RIBOFLAVIN CONTENT OF GRAINS GROUPED ACCORDING TO YEAR

Year	No. of samples	Mean protein, %	Vitamin, $\mu\text{gm.}/\text{gm.}$	
			Mean	S.d.
<i>Thiamine</i>				
Marquis wheat				
1944	17	12.8	3.82	0.74
1945	14	14.4	5.11	0.98
	31	13.5	4.40	1.20
Newal barley				
1944	22	12.3	4.59	1.15
1945	21	13.9	4.60	0.90
	43	13.1	4.60	1.02
Victory oats				
1944	26	10.9	5.35	1.41
1945	24	12.6	5.84	1.61
	50	11.7	5.58	1.51
<i>Riboflavin</i>				
Marquis wheat				
1944	20	12.9	1.25	0.15
1945	14	14.4	1.45	0.27
	34	13.5	1.34	0.23
Newal barley				
1944	26	12.4	1.25	0.28
1945	21	13.9	1.24	0.22
	47	13.1	1.25	0.25
Victory oats				
1944	26	10.9	1.21	0.09
1945	24	12.6	1.35	0.22
	50	11.7	1.27	0.18

reported by Whiteside and Jackson (16) as the mean for a large number of samples of wheat grown in Western Canada. The mean thiamine values obtained for Newal barley and Victory oats are somewhat lower than others that have been reported for barley and oats grown in the United States (4, 10, 11). The riboflavin assay results are similar to those obtained by Andrews, Boyd, and Terry (2), who report means of 1.32 $\mu\text{gm.}$ per gm. for riboflavin in Marquis wheat grown at four different stations in Minnesota, and means of 1.21 and 1.30 $\mu\text{gm.}$ per gm. for riboflavin in six varieties of barley and five varieties of oats, respectively.

Application of the *t* test to the present data showed that the difference between the mean thiamine content of the oat samples and that of wheat or

barley is significant beyond the 1% point. The differences between the three cereals in riboflavin content are not statistically significant.

The relation between protein and thiamine content was studied by grouping all the thiamine assay values for each of the three grains without regard to year or origin. It is shown in Table IV that a highly significant positive correlation was found to exist between protein and thiamine in wheat and oats but not in barley. Scatter diagrams for each of the three grains are

TABLE IV
CORRELATION COEFFICIENTS BETWEEN PROTEIN AND THIAMINE
IN WHEAT, BARLEY, AND OATS

Cereal	D.f.	<i>r</i>	5% pt.	1% pt.
Marquis wheat	29	0.513**	0.356	0.456
Newal barley	41	0.266	0.301	0.389
Victory oats	48	0.652**	0.279	0.361

** Significant beyond 1% point.

given in Fig. 2. A similar analysis of the riboflavin results indicated that there was no significant correlation between protein and riboflavin in any of the three cereals.

In an attempt to assess the effect of soil zone on the thiamine and riboflavin content of wheat, barley, and oats, the data were grouped and analyzed according to soil zones and years, as shown in Tables V and VI. Reference to Table V shows that the mean thiamine content of all three grains was lowest for samples grown on gray soils, intermediate for those from black soils, and highest for those grown on brown soils. The existence of this soil zone-thiamine relation in all three grains is interesting, since the barleys assayed differed from the wheat and oats in that they failed to demonstrate a significant correlation between protein and thiamine. This suggests that soil zone may have more effect on thiamine accumulation than has protein content as such.

The results of analysis of variance (Table VI) indicate that, in general, the soil zone-thiamine relations suggested by the data in Table V are statistically significant. However, the variability in the thiamine content of individual samples within a given zone was so great that the accuracy of estimates of thiamine levels in grains based on soil zone-thiamine correlations is not likely to be high. Nonetheless, the fact that further analysis of the data as summarized in Table VII shows that for all three grains the mean thiamine content of the samples grown on brown soils was significantly higher than that of samples grown on gray soils suggests that soil zone-thiamine relations may be of practical significance when grains grown on widely different types of soil and under markedly different climatic conditions are under consideration. The differences between mean thiamine levels in grains grown under some-

what more similar conditions were not so marked. Thus, differences between the mean thiamine content of samples grown on black soil and those grown on gray soil were highly significant only in the case of oats, while for the brown-black soil zone comparison highly significant differences existed only in wheat.

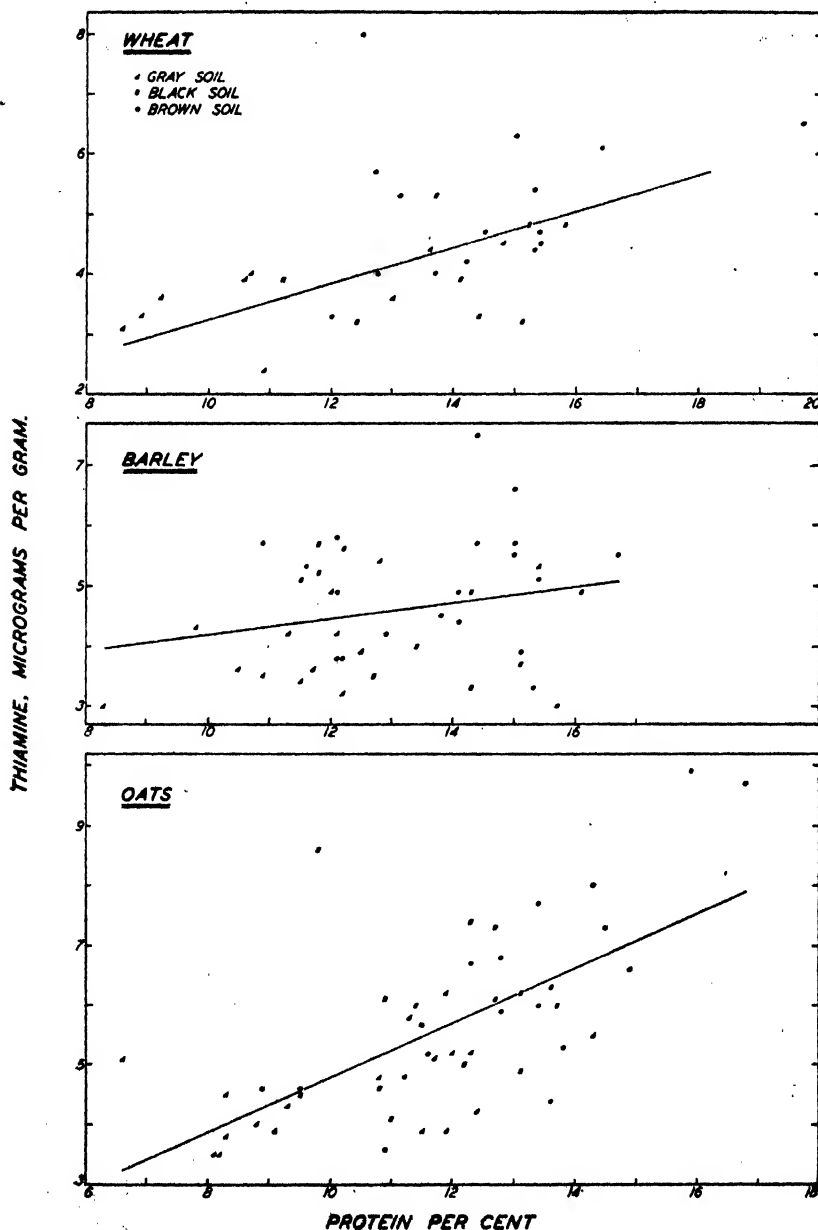


FIG. 2. Relation between thiamine and protein content of grains.

TABLE V

THIAMINE AND RIBOFLAVIN CONTENT OF GRAINS GROUPED ACCORDING TO SOIL ZONES AND YEARS

Soil zone	Marquis wheat				Newal barley				Victory oats			
	No. of samples	Mean protein, %	Vitamin, μ gm./gm.		No. of samples	Mean protein, %	Vitamin, μ gm./gm.		No. of samples	Mean protein, %	Vitamin, μ gm./gm.	
			Mean	S.d.			Mean	S.d.			Mean	S.d.
Thiamine												
Gray and gray transition												
1944	7	10.9	3.50	0.66	6	11.0	3.60	0.67	9	9.4	4.46	0.76
1945	2	12.0	4.10	—	7	12.1	4.40	0.77	10	11.5	4.84	0.94
	9	11.1	3.6	0.66	13	11.6	4.04	0.77	19	10.5	4.65	0.86
Black and shallow black												
1944	5	14.1	3.68	0.69	7	12.7	4.76	0.97	9	11.7	5.52	0.98
1945	3	14.5	4.67	0.71	3	14.9	4.15	0.63	4	12.2	7.05	1.30
	8	14.2	4.05	0.83	10	13.3	4.59	0.89	13	11.9	5.99	1.25
Brown and dark brown												
1944	5	14.2	4.36	0.72	9	12.8	5.12	1.19	8	11.8	6.15	1.88
1945	9	14.8	5.50	1.41	11	14.8	4.85	1.04	10	13.8	6.36	1.76
	14	14.7	5.09	1.30	20	13.9	4.97	1.09	18	12.9	6.27	1.76
Riboflavin												
Gray and gray transition												
1944	7	10.9	1.18	0.16	6	11.0	1.06	0.24	9	9.4	1.16	0.10
1945	2	12.0	1.28	—	7	12.1	1.28	0.27	10	11.5	1.22	0.24
	9	11.1	1.20	0.15	13	11.6	1.18	0.27	19	10.5	1.19	0.11
Black and shallow black												
1944	6	13.8	1.25	0.23	10	13.0	1.31	0.26	9	11.7	1.20	0.09
1945	3	14.5	1.37	0.62	3	14.9	1.55	0.23	4	12.2	1.54	0.13
	9	14.1	1.40	0.39	13	13.5	1.36	0.27	13	11.9	1.31	0.19
Brown and dark brown												
1944	7	14.3	1.33	0.13	10	12.5	1.30	0.30	8	11.8	1.26	0.09
1945	9	14.8	1.41	0.13	11	14.8	1.14	0.05	10	13.8	1.39	0.17
	16	14.6	1.38	0.13	21	13.7	1.21	0.22	18	12.9	1.33	0.15

Thiamine surveys done by Johansson and Rich (9) on commercial Western Canadian wheats grown in 1940 and by Hoffer, Alcock, and Geddes (7) on the 1941 crop failed to demonstrate a significant effect of soil zone on thiamine content although the results obtained in the latter survey did suggest that a relation between thiamine and soil zone might exist inasmuch as it was found

TABLE VI
ANALYSIS OF VARIANCE FOR THIAMINE AND RIBOFLAVIN

Variance due to	Wheat		Barley		Oats	
	D.f.	Mean square	D.f.	Mean square	D.f.	Mean square
<i>Thiamine</i>						
Soil zone	2	6.42**	2	3.42**	2	13.43**
Year	1	12.91**	1	0.00	1	3.06
Error	27	0.650	39	0.946	46	1.775
Total	30		42		49	
<i>Riboflavin</i>						
Soil zone	2	0.166*	2	0.127	2	0.98*
Year	1	0.220*	1	0.00	1	0.248**
Error	30	0.044	43	0.062	46	0.026
Total	33		46		49	

* Significant beyond the 5% point.

** " " " 1% "

TABLE VII

t VALUES DERIVED TO TEST THE SIGNIFICANCE OF DIFFERENCES IN THE MEAN THIAMINE CONTENT OF SAMPLES GROWN ON DIFFERENT TYPES OF SOIL

	Wheat		Barley		Oats	
	No. of samples	<i>t</i>	No. of samples	<i>t</i>	No. of samples	<i>t</i>
Between soil zones:						
Black-gray	17	1.77	23	2.24*	32	5.11**
Brown-gray	23	5.40**	33	3.96**	37	5.66**
Brown-black	22	3.26**	30	1.45	31	0.74

* Significant beyond the 5% point.

** " " " 1% "

that wheat samples from the dark brown soil zone of Saskatchewan were significantly higher in thiamine than those from the other soil zones.

With reference to the data in Table VI for variance due to year, it must be pointed out that the significance of these data is impaired by the fact that only about 30% of the wheat samples and 50% of the barley and oat samples were grown in the same locations in both years. With this limitation in mind, the results indicate that the mean thiamine content of the oat and barley samples grown in 1944 was essentially the same as that of those grown

in 1945. On the other hand, the wheat samples from the 1945 crop were significantly richer in thiamine than those grown in 1944. It seems unlikely that the higher level of thiamine in the 1945 wheat can be attributed to the higher protein content of these samples, since the three grains showed essentially the same seasonal difference in protein levels.

With regard to the results for riboflavin, it would appear from the data in Tables V and VI that the probability of the existence of significant differences in vitamin content of grain attributable to soil zone is less for riboflavin than for thiamine. As has been mentioned, the significance of the data for the effect of year is limited but it is interesting to note that for all three soil zones the riboflavin content of the oat samples grown in 1945 was appreciably greater than that of those grown in the preceding year.

Acknowledgment

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THE NIACIN CONTENT OF WHEAT, BARLEY, AND OATS GROWN IN DIFFERENT SOIL ZONES IN ALBERTA¹

L. W. McELROY² AND H. SIMONSON³

Abstract

Microbiological niacin assays were done on 34 samples of Marquis wheat, 48 of Newal barley, and 50 of Victory oats grown on gray, black, and brown soils in the years 1944 and 1945. Mean values of 53.6, 70.4, and 10.3 $\mu\text{gm.}$ of niacin per gram were obtained for wheat, barley, and oats respectively. Although these results suggest that Newal barley may contain more niacin than does Marquis wheat, the results of assays conducted by a chemical method indicate that there is little difference in the mean niacin content of these two grains. Niacin levels were found to be highly variable in all three grains. Niacin and protein levels were found to be positively correlated in wheat and oats while in barley a tendency towards an inverse relation between niacin and protein was observed. No evidence was obtained to indicate that the type of soil on which grains are grown has any marked effect on the accumulation of niacin. The wheat and oat samples from the 1945 crop were richer in both niacin and protein than those from the 1944 crop, while barley samples from the 1945 crop, although richer in protein than those grown the preceding year, contained essentially the same amount of niacin.

Introduction

Recognition of the importance of niacin in swine and poultry nutrition in addition to its established role in the prevention and cure of pellagra has stimulated interest in the distribution of this vitamin in cereal grains used in livestock feeds. Hale, Davis, and Baldwin (6) have reported ranges of 60 to 96, 60 to 81, and 18 to 21 $\mu\text{gm. per gm.}$ in wheat, barley, and oats respectively, while Davis, Laufer and Saletan (4) list values of 49.3 to 66.1 and 69.0 to 98.1 $\mu\text{gm. per gm.}$ for samples of wheat and barley of different origin and variety. Brown, Thomas, and Bina (3) have stressed the importance of existing discrepancies in niacin assay values associated with variations in methods of preparation and assay of different materials. The present study was made to:— (1) obtain information on the relative niacin content of wheat, barley, and oats grown under widely different conditions of soil and climate in the province of Alberta, and (2) study possible correlations between protein and niacin content and between soil type and niacin levels in each of these cereal grains.

Experimental

Assay Material

The grains studied were Marquis wheat, Newal barley, and Victory oats. The samples used were the same as those described by McElroy, Kastelic, and McCalla (8).

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Assay Methods

Protein

Nitrogen was determined by the Kjeldahl method with mercuric oxide as catalyst. Protein in wheat is reported as nitrogen $\times 5.7$ and in oats and barley as nitrogen $\times 6.25$. All protein and vitamin assay results are expressed on the basis of 13.5% moisture.

Niacin

In preliminary studies, niacin assay values obtained by the chemical method of Melnick, Oser, and Siegel (9) and by the microbiological procedure of Krehl, Strong, and Elvehjem (7) were compared. In Table I it is shown that the mean results obtained for wheat and oats by the two methods are in good agreement, while for barley the mean microbiological values are approximately 15% higher than those obtained by the chemical method.

TABLE I
CHEMICAL AND MICROBIOLOGICAL NIACIN ASSAY VALUES

Cereal	Number of samples	Mean protein, %	Procedure			
			Chemical		Microbiological	
			Niacin, $\mu\text{gm.}/\text{gm.}$		Niacin, $\mu\text{gm.}/\text{gm.}$	
			Mean	Range	Mean	Range
Wheat	23	14.0	60.8	50.2 - 78.1	59.6	45.7 - 72.3
Oats	28	12.7	13.5	9.5 - 22.6	12.1	8.0 - 18.7
Barley	24	13.8	62.1	48.9 - 74.3	71.2	58.7 - 87.3

A few assays were done on barley to compare results obtained chemically by a modification of the collaborative method described by Steele (10) and microbiologically on extracts treated with Lloyd's reagent, lead nitrate, and hydrogen peroxide as suggested by the reports of Brown, Thomas, and Bina (2, 3) who have demonstrated that treatment of extracts with hydrogen peroxide materially lowers the apparent niacin content of a number of materials as measured by microbiological methods.

The results shown in Columns 2 and 3 of Table II were obtained by the following procedures.

A two gram sample was weighed and suspended in 75 ml. of 2 *N* sulphuric acid in a 100 ml. volumetric flask. After hydrolysis in boiling water for one hour the flask was cooled and made up to volume with distilled water. The contents was well mixed and two 25 ml. aliquots, one for chemical and one for microbiological assay, were transferred to 50 ml. centrifuge tubes. Adsorption on Lloyd's reagent, elution with sodium hydroxide, and decolorization with lead nitrate were carried out for both tubes according to the method described by Steele (10). The niacin content of the extract from the first tube

was determined by the color development method of Melnick, Oser, and Siegel (9). Prior to microbiological assay the extract from the second tube was treated with 5 ml. of 40% sodium hydroxide and 5 ml. of 30% hydrogen peroxide at a temperature of 70° C. for two hours and then evaporated to dryness on a steam bath. The residue was dissolved in distilled water, adjusted to pH 6.8, and diluted to the original volume. The oxidized extract was assayed by the microbiological method of Krehl, Strong, and Elvehjem (7). The values obtained on three samples of barley are shown in Columns 2 and 3 of Table II. For comparison, the values obtained by the unmodified methods

TABLE II
BARLEY NIACIN ASSAY VALUES OBTAINED BY DIFFERENT METHODS

Sample	(1) Chemical, Melnick <i>et al.</i>	(2) Chemical following treatment with Lloyd's reagent and $\text{Pb}(\text{NO}_3)_2$	(3) Microbiological following treatment with Lloyd's reagent, $\text{Pb}(\text{NO}_3)_2$, and H_2O_2	(4) Microbiological, Krehl <i>et al.</i>
	$\mu\text{gm. per gm.}$			
B--1	52	34	36	63
B--2	66	40	45	77
B--3	68	43	48	75

of Melnick *et al.* and Krehl *et al.* are given in Columns 1 and 4. These results are in general agreement with those of Brown, Thomas, and Bina (3) who stress the importance of variations in apparent niacin values as determined by microbiological and chemical methods and point out the need for data on available niacin, derived from bioassays, to provide a sound basis for the interpretation of microbiological and chemical assay results.

The assay values given in the body of the present report were obtained by the microbiological method of Krehl, Strong, and Elvehjem (7). Although it is recognized that these values may not constitute an accurate measure of biologically available niacin in grains, particularly in wheat and barley, this method was adopted in preference to the chemical procedure of Melnick, Oser, and Siegel (9) owing to the fact that difficulty was experienced in obtaining reproducible results with different batches of cyanogen bromide, and in preference to methods involving adsorption and elution, because such methods are tedious for routine use.

Results

Comparative Niacin Content of Wheat, Barley, and Oats

The results of microbiological niacin assays done on 34 samples of Marquis wheat, 48 of Newal barley, and 50 of Victory oats grown under a wide variety of soil and climatic conditions in the province of Alberta during the years 1944 and 1945 are summarized in Table III.

TABLE III
 NIACIN CONTENT OF GRAINS GROUPED ACCORDING TO YEAR

Year	No. of samples	% Protein, mean	Niacin, $\mu\text{gm./gm.}$	
			Mean	S. d.
<i>Marquis wheat</i>				
1944	20	12.9	50.8	7.6
1945	14	14.4	57.6	6.2
	<u>34</u>	<u>13.5</u>	<u>53.6</u>	<u>7.8</u>
Range			41.3 - 74.0	
<i>Nearl barley</i>				
1944	26	12.4	69.9	11.3
1945	22	14.1	71.1	7.6
	<u>48</u>	<u>13.2</u>	<u>70.4</u>	<u>9.7</u>
Range			49.3 - 99.3	
<i>Victory oats</i>				
1944	26	10.9	8.7	1.9
1945	24	12.6	12.0	2.4
	<u>50</u>	<u>11.7</u>	<u>10.3</u>	<u>2.7</u>
Range			7.0 - 17.0	

When the extreme variations that exist in the niacin content of different samples of all three grains are taken into consideration, the mean niacin values of 53.6, 70.4, and 10.3 $\mu\text{gm. per gm.}$ for wheat, barley, and oats respectively are in reasonably good agreement with those obtained on smaller numbers of samples by other workers (1, 4, 6, 11). Application of the *t* test to the present data showed that the difference between the mean niacin content of wheat and barley is highly significant, but in view of the uncertainty that exists (2, 3, 5) regarding the accuracy of microbiological niacin assay values as an index of biologically available niacin in these grains it is questionable whether barley should be ranked above wheat as a source of niacin. In this connection it may be noted that, as is shown in Table I, the mean niacin assay values for 23 samples of wheat and 24 samples of barley, as determined by the chemical procedure of Melnick, Oser, and Siegel (9), were approximately the same.

Niacin - Year Relations

It is shown in Table III that the mean niacin content of wheat samples grown in 1945 was approximately 13% higher than that of those grown in

1944. The corresponding figures for barley and oats are 2% and 38% respectively. Analysis of the data showed that for wheat and oats these differences are significant beyond the 1% point. While definite conclusions cannot be drawn from such limited data, the results suggest that significant variations may exist in the niacin content of wheat and oats grown in different years.

Niacin-Protein Relations

Inspection of Fig. 1 and Table IV shows that, although protein content was not a reliable index of the niacin content of wheat or oats, niacin and protein levels were found to be positively correlated in these grains. The

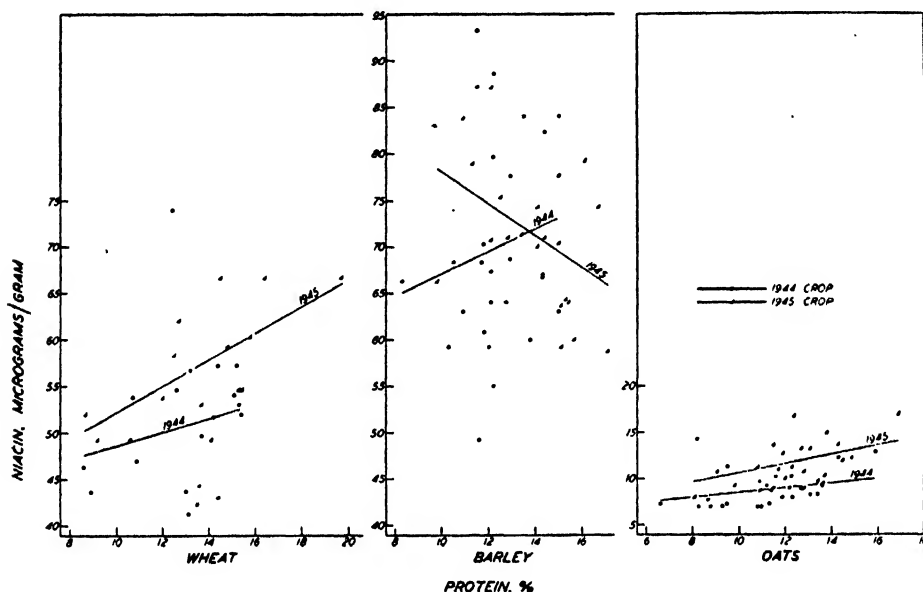


FIG. 1. Relation between niacin and protein content of grains.

TABLE IV

CORRELATION COEFFICIENTS BETWEEN NIACIN AND PROTEIN IN WHEAT, BARLEY, AND OATS

Cereal	Year	D. f.	<i>r</i>	5% pt.	1% pt.
Marquis wheat	1944	18	+ .196	.444	.562
	1945	12	+ .644*	.533	.662
	Both years	32	+ .422*	.357	.437
Newal barley	1944	24	+ .167	.388	.496
	1945	20	- .445*	.424	.536
	Both years	46	- .048	.285	.369
Victory oats	1944	24	+ .298	.387	.496
	1945	22	+ .410*	.403	.515
	Both years	48	+ .488**	.279	.361

contrast between the niacin \times protein correlation coefficients derived for Marquis wheat and Victory oats and those derived for Newal barley is interesting, and in this connection it may be mentioned that the niacin \times protein correlation coefficient derived for eight samples of barley grown in 1946 was -0.206 . Although neither this value nor the -0.048 coefficient for the total of 48 samples from the 1944 and 1945 crops is statistically significant, the results suggest that a tendency towards an inverse relation between niacin and protein may exist in barley.

Niacin - Soil Zone Relations

The effect of soil zone on the niacin content of wheat, barley, and oats was studied by grouping the data as summarized in Table V. It is apparent from the data in this table that differences in the mean niacin content of grains grown on different types of soil were relatively small and that the variability within any one soil zone was high. Analysis of the data showed that the difference between the mean of $57.4 \mu\text{gm.}$ of niacin per gram for nine samples of Marquis wheat grown on black or shallow black soil and the mean of $48.5 \mu\text{gm.}$ for nine samples grown on gray or gray transition soil is significant beyond the 1% point, but none of the other differences in mean niacin levels attributable to soil zone (Table V) were found to be statistically significant.

TABLE V

SUMMARY OF THE NIACIN CONTENT OF 1944 AND 1945 WHEAT, BARLEY, AND OAT SAMPLES, GROUPED ACCORDING TO SOIL ZONE

Year	Marquis wheat				Newal barley				Victory oats			
	No. samples	Mean protein, %	Niacin, $\mu\text{gm.}/\text{gm.}$		No. samples	Mean protein, %	Niacin, $\mu\text{gm.}/\text{gm.}$		No. samples	Mean protein, %	Niacin, $\mu\text{gm.}/\text{gm.}$	
			Mean	S.d.			Mean	S.d.			Mean	S.d.
Gray and gray transition soil zone												
1944	7	10.9	46.9	3.6	6	11.0	71.5	10.1	9	9.4	8.4	2.5
1945	2	12.0	54.3	7.1	7	12.1	72.9	6.9	10	11.5	12.0	2.4
	9	11.1	48.5	5.2	13	11.6	72.3	8.2	19	10.5	10.3	3.0
Black and shallow black soil zone												
1944	6	13.8	59.0	7.5	10	13.0	73.5	11.3	9	11.7	8.4	1.0
1945	3	14.5	54.2	5.6	3	14.9	71.4	7.8	4	12.2	12.6	2.1
	9	14.0	57.4	6.9	13	13.4	73.0	10.6	13	11.9	9.7	2.4
Brown and dark brown soil zone												
1944	7	14.2	47.6	5.1	10	12.5	65.3	11.0	8	11.8	9.5	1.9
1945	9	14.1	59.5	6.1	12	15.0	70.0	8.8	10	13.8	11.7	2.8
	16	14.1	54.3	8.2	22	13.9	67.9	9.9	18	12.9	10.7	2.6

Discussion

From the present data for niacin in samples of wheat, barley, and oats and those reported by McElroy, Kastelic, and McCalla (8) for thiamine and riboflavin in the same samples, comparisons may be drawn between three species of grain and between three vitamins with respect to the degree of association that appears to exist between vitamin and protein levels in grains and between vitamin content and the type of soil on which grains are grown. The data indicate that although thiamine and protein levels tend to be positively correlated in all three grains the relation is much closer in wheat and oats than in barley. It would appear that niacin levels also tend to vary directly with protein levels in wheat and oats, while in barley there is some evidence that an inverse relation may exist between niacin and protein. The data for riboflavin fail to demonstrate the existence of any correlation between levels of this vitamin and protein in wheat, barley, or oats.

Variations in vitamin levels that may be associated with soil zones seem to be more marked for thiamine than for either riboflavin or niacin. Although some of the differences were small the mean thiamine content of all three grains was found to be highest in samples grown on brown soils, intermediate in those grown on black soils, and lowest in those from the gray soil zone. The data for riboflavin-soil zone relations are less conclusive, although they do provide some evidence to suggest that in wheat and oats riboflavin levels may tend to be slightly lower in samples grown on gray soils than in those grown in either black or brown soil zones. In the case of niacin, no uniform trend that would suggest the existence of a close association between soil type and levels of this vitamin in grains was observed.

Acknowledgments

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ANTIFREEZE PROPERTIES OF TETRAHYDROFURFURYL ALCOHOL AND ANHYDROUS GLYCOL SOLUTIONS¹

BY K. A. CLENDENNING²

Abstract

Tetrahydrofurfuryl alcohol remains mobile at -75°C . in the presence of 0 to 20% water. It has a lower heat capacity, surface tension, and flash point than ethylene glycol, and undergoes almost identical expansion on heating. Its aqueous solutions exhibit maxima in specific gravity and viscosity at solute concentrations of 80 to 90% but do not distil azeotropically. Swelling and softening of immersed natural and synthetic rubber compounds were more serious with tetrahydrofurfuryl alcohol than with ethylene glycol, but only small differences were shown by radiator hose connections after lengthy immersion and driving tests. The viscosity of anhydrous glycol blends having freezing points of -50°C . varies greatly with the glycol employed as second component, ethylene glycol - trimethylene glycol being the least viscous of the six binary glycol solutions studied. Substitution of tetrahydrofurfuryl alcohol for the second glycol component reduces the viscosity but necessitates use of higher concentrations for equivalent freezing point lowering.

Introduction

The most interesting development in engine coolants during the decade preceding World War II pertained to the use of pure ethylene glycol as a high temperature coolant for aircraft (10, 16). According to Cox and Clapsaddle (7, 8), the liquid range of ethylene glycol is greatly extended in this application by the addition of a second glycol. Information was not provided, however, on the relative suitability of the glycols mentioned in the Cox patents or of the many that have since become available in commercial quantities. Although anhydrous ethylene glycol or glycol blends have not been used extensively as high temperature coolants, demonstration of the advantages of high temperature liquid cooling paved the way for the pressurized glycol-water cooling systems (9) of service aircraft and ground vehicles as well as of certain postwar automobiles.

Cairns (2) and Schenck and Gellendien (17) have claimed the use of tetrahydrofurfuryl alcohol (T.H.F.A.) as a freezing point depressant for water and as a component of ternary aqueous systems. The information provided by them was limited to freezing point data and did not indicate superiority over compounds then in use. According to Cairns (2), the

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viscosity of aqueous glycerol solutions is lowered by the addition of tetrahydrofurfuryl alcohol. Freezing point data for tetrahydrofurfuryl alcohol – glycerol – water showed, however, that the freezing point increased with progressive substitution of tetrahydrofurfuryl alcohol for glycerol (2). Corresponding data were not provided on the viscosity changes, and the value of tetrahydrofurfuryl alcohol in this application has accordingly remained uncertain. As a third component for use with aqueous *l*-2,3-butanediol, tetrahydrofurfuryl alcohol actually proved less effective as an accessory freezing point depressant and thinning agent than methanol, ethanol, or ethylene glycol (6).

The present investigation was undertaken to assess the usefulness of tetrahydrofurfuryl alcohol as an antifreeze when used alone, and when mixed with water or with anhydrous glycols of low molecular weight. A series of anhydrous glycol mixtures was also investigated with respect to freezing point and viscosity at low temperatures.

Materials and Methods

With the exception of *levo*-2,3-butanediol*, the chemicals employed in this study were obtained from the Eastman Kodak Laboratories. The polyethylene glycols and dipropylene glycol were used as received. *dl*-Tetrahydrofurfuryl alcohol, *levo*-2,3-butanediol, ethylene glycol, propylene glycol, and trimethylene glycol were redistilled *in vacuo*, employing an 18 in. Stedman column. The solutions were freshly prepared by accurate weighing and their compositions are expressed on this basis.

Specific heat measurements were made by the electrical heating method described by Clark, Waldeland, and Cross (3). The adopted stirring rate caused a maximum of 0.05° C. temperature change during the five minute heating period. The furfuryl alcohol content of tetrahydrofurfuryl alcohol was determined by applying the Hughes and Acree bromine method for furfural (13) to 20-gm. samples. Contents of 0.03 to 0.07% were shown by the tetrahydrofurfuryl alcohol samples employed in these studies. The remaining methods have been described in earlier papers (4-6).

Values for the boiling point and refractive index for tetrahydrofurfuryl alcohol that have been reported previously show good agreement with the present observations (Table I). Constant boiling mixtures were not obtained by distillation of dilute aqueous solutions. The density values of Table I differ considerably, our data showing closest agreement with that of Wienhaus (18).

Results

The data of Fig. 1 show that tetrahydrofurfuryl alcohol is decidedly less effective than ethylene glycol as a freezing point depressant for water at solute concentrations of 10 to 60%. When the solute concentration is 80% or higher, the freezing point of tetrahydrofurfuryl alcohol – water is below

* Prepared in the divisional pilot plant.

TABLE I

PHYSICAL CONSTANTS FOR TETRAHYDROFURFURYL ALCOHOL

	Heilbron (12)	Wienhaus (18)	Balfe <i>et al.</i> (1)	Handbook of chemistry and physics	Author's observations
Density	D_4^{25} 1.1326	D_4^{20} 1.0544		D_4^{20} 1.0495	D_4^{20} 1.0587 $D_4^{37.8}$ 1.0490
Refractive index	n_D^{25} 1.4505	n_D^{20} 1.4517	n_D^{16} 1.4529	n_D^{19} 1.4502	n_D^{25} 1.4507
Boiling point, ° C.		177 at 750 mm. 85-86 at 26 mm.	177.9	177-8 at 743 mm.	178 at 760 mm. 105 at 72 mm. 86 at 26 mm.

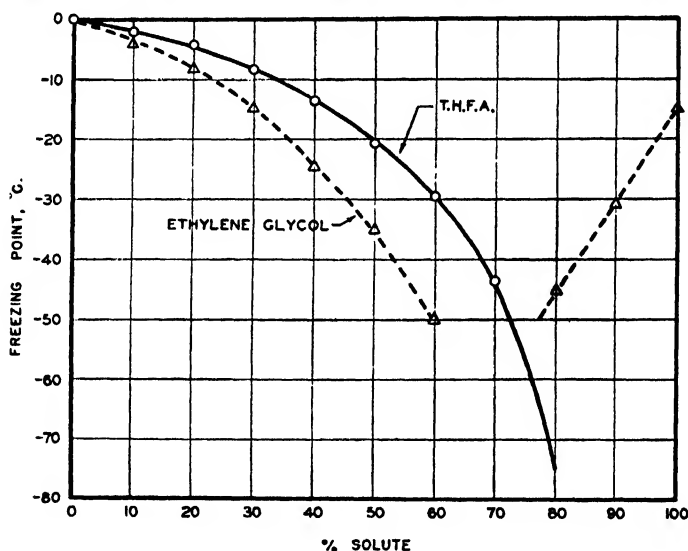


FIG. 1. Freezing points of aqueous tetrahydrofurfuryl alcohol and of aqueous ethylene glycol solutions.

-70° C. (-100° F.). Pure tetrahydrofurfuryl alcohol could not be induced to crystallize even at the temperature of liquid air. The freezing point of ethylene glycol-water rises sharply as the solute concentration is increased from 70 to 100%. At 80, 90, and 100% concentrations, the additional protection against freezing that is provided by tetrahydrofurfuryl alcohol amounts to 30°, 45°, and 60° C., respectively. Evaporation of water or addition of the pure solute does not lead to diminished protection with concentrated aqueous tetrahydrofurfuryl alcohol solutions as in the case of eutectic ethylene glycol-water mixtures.

Figs. 2 and 3 present freezing point data for anhydrous glycol solutions. From these it may be seen that ethylene glycol is definitely superior to *levo*-2,3-butanediol as a component of anhydrous antifreeze mixtures. Higher

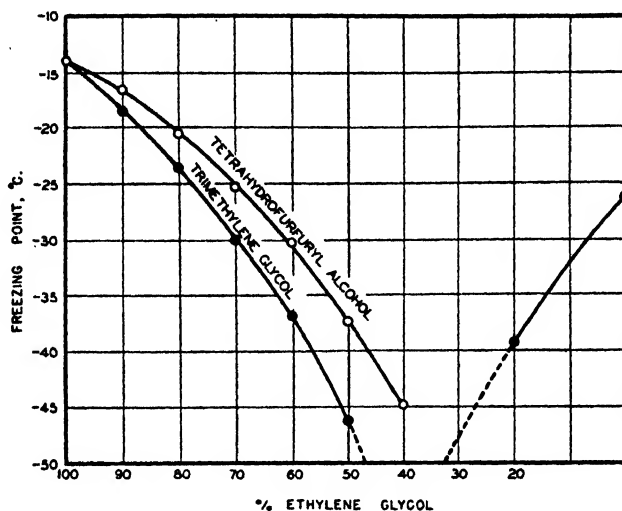


FIG. 2. Freezing points of anhydrous ethylene glycol solutions.

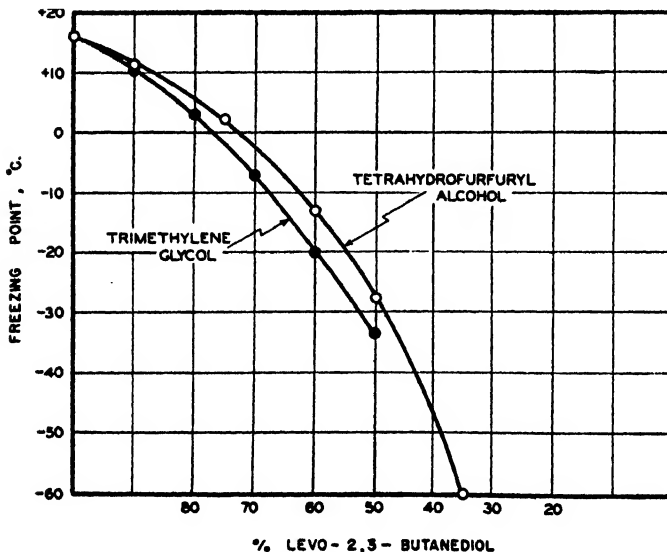


FIG. 3. Freezing points of anhydrous l-2,3-butanediol solutions.

proportions of tetrahydrofurfuryl alcohol are required in reducing the freezing point of ethylene glycol than when glycols of low molecular weight, such as trimethylene glycol, are employed. Freezing point determinations on glycol-polyethylene glycol blends indicated no advantage for deviations

from the 1 : 1 proportion recommended by Cox (7). The freezing points of anhydrous tetrahydrofurfuryl alcohol - glycol blends on the other hand were reduced to very low temperatures when the concentration of tetrahydrofurfuryl alcohol was increased beyond 50%.

The glycol blends referred to in Fig. 4 show higher viscosity values at -10°C. than pure ethylene glycol and are extremely viscous at low temperatures. Kinematic viscosity values of 1000 and 500 centistokes are attained

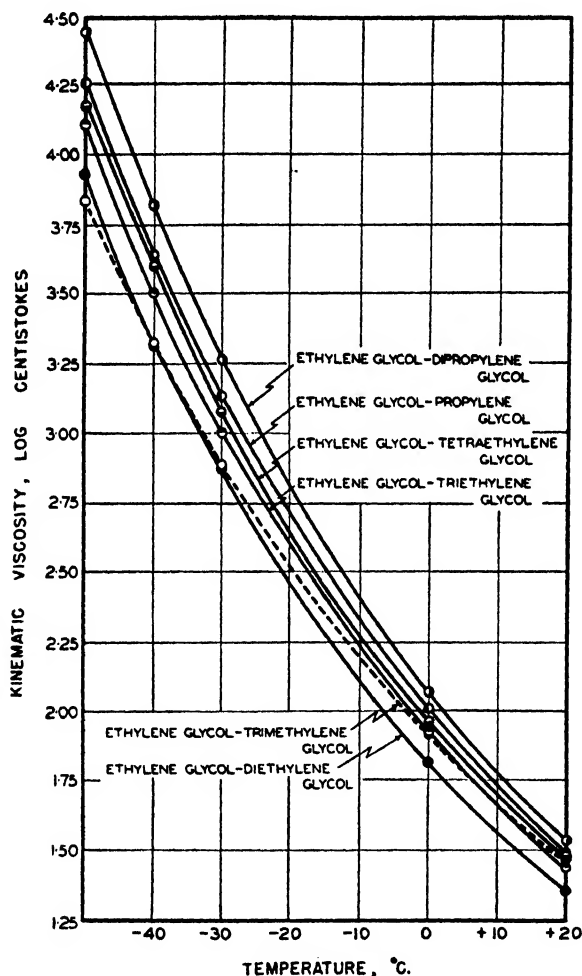


FIG. 4. Kinematic viscosity of anhydrous ethylene glycol solutions (1 : 1) at low temperatures.

by these systems at -24° to -33.5°C. and at -17.5° to -27°C. , respectively. The polyethylene glycol blends are less viscous than those prepared with propylene or dipropylene glycol, and, within the polyethylene glycols, the expected relation to molecular size is exhibited. The data of Fig. 4 also

indicate an interesting effect of position isomerism: at -40° to -50° C., ethylene glycol – propylene glycol (1,2-propanediol) is one of the most viscous, whereas ethylene glycol – trimethylene glycol (1,3-propanediol) is the least viscous of the blends reported in this figure.

The particular point of interest in the data of Fig. 5 is that all the tetrahydrofurfuryl alcohol solutions show considerably lower viscosity values than pure ethylene glycol between $+20^{\circ}$ and -10° C. 80% tetrahydrofurfuryl

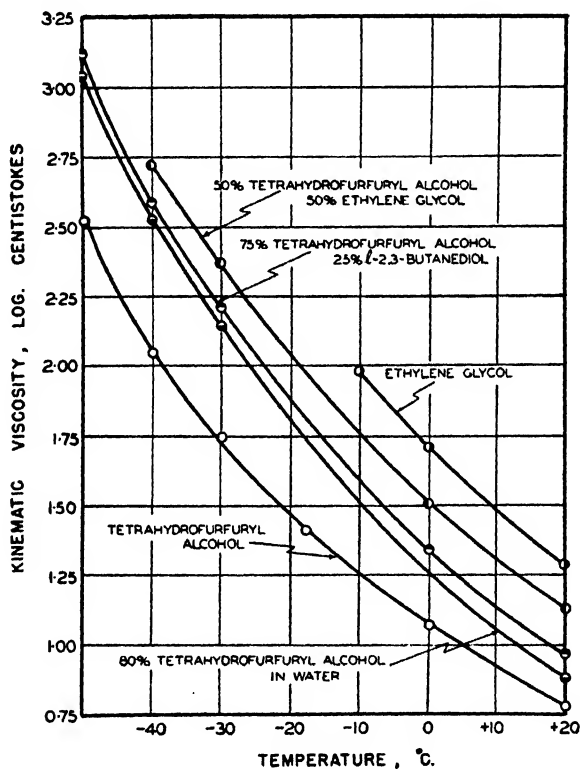


FIG. 5. Kinematic viscosity of tetrahydrofurfuryl alcohol and of tetrahydrofurfuryl alcohol solutions at low temperatures.

alcohol – 20% water is considerably more viscous than pure tetrahydrofurfuryl alcohol at low temperatures. Kinematic viscosity data presented elsewhere (4) show that 60% ethylene glycol – 40% water is less viscous than 80% tetrahydrofurfuryl alcohol – 20% water and more viscous than pure tetrahydrofurfuryl alcohol between -20° and -50° C.

Aqueous tetrahydrofurfuryl alcohol solutions at 20° C. exhibit a maximum in kinematic viscosity at a concentration of 80 to 90% by weight or with equimolar proportions of the two components (Fig. 6). The corresponding absolute viscosity values (centipoises) show similar changes with concentration: 100% tetrahydrofurfuryl alcohol, 6.24; 90%, 7.89; 80%, 7.85; 60%, 5.77;

40%, 3.56; 20%, 1.92. It should be noted that viscosity maxima are also exhibited by aqueous solutions of methanol, ethanol, propanol, allyl alcohol, and of certain monocarboxylic acids (14), but are not shown by glycols (15) or by dicarboxylic acids (14).

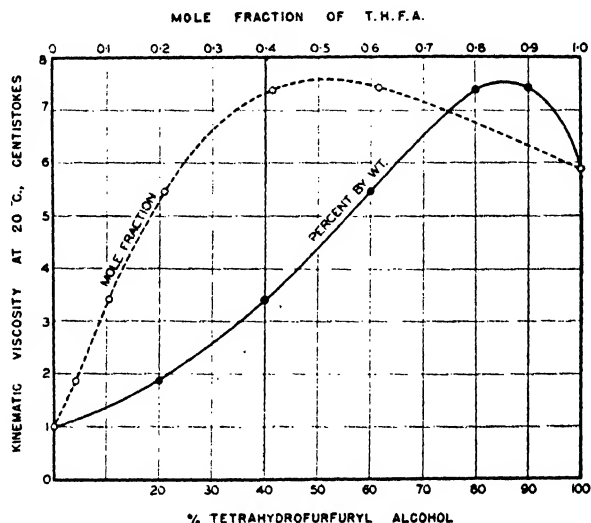


FIG. 6. Kinematic viscosity of aqueous tetrahydrofurfuryl alcohol solutions at 20° C.

Aqueous tetrahydrofurfuryl alcohol solutions also attain a maximum in specific gravity at a concentration of 80 to 90% (Fig. 7). Since a simple

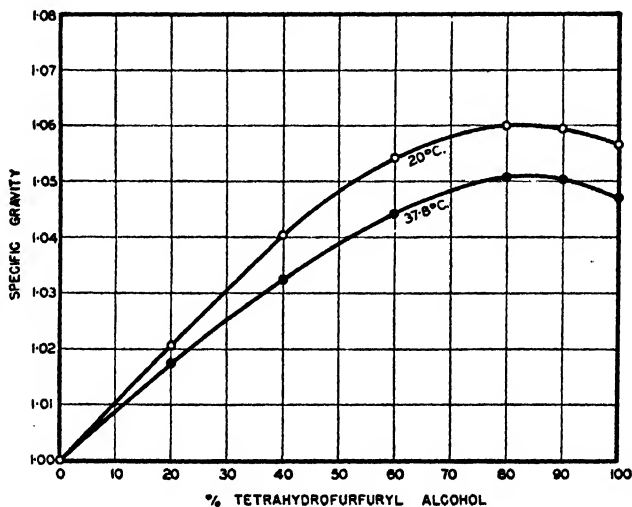


FIG. 7. Specific gravity of aqueous tetrahydrofurfuryl alcohol solutions at 20° and 37.8° C.

relation does not exist between tetrahydrofurfuryl alcohol concentration and density, hydrometers are less suitable for the practical testing of tetrahydrofurfuryl alcohol solutions than of currently used antifreeze mixtures. Density

maxima are similarly shown by aqueous solutions of glycols above ethylene glycol, i.e., propane-, butane- and pentanediol position isomers (15), but not by aqueous solutions of ethylene glycol or of monohydric alcohols having relatively low molecular weights.

Table II indicates that thermal expansion remains relatively constant at tetrahydrofurfuryl alcohol contents of 60 to 100%. Considerable contraction occurs on mixing tetrahydrofurfuryl alcohol with water and heat is evolved.

TABLE II

REFRACTIVE INDEX, THERMAL EXPANSION, AND CONTRACTION ON MIXING OF
AQUEOUS TETRAHYDROFURFURYL ALCOHOL SOLUTIONS

% T.H.F.A. by weight	Refractive index at 25° C.	Thermal expansion 20°–37.8° C. $\alpha \times 10^{-3}$	Contraction on mixing, ml. per 100 ml. initial volume	
			20° C.	37.8° C.
40	1.3834	0.44	2.01	1.97
60	1.4080	0.54	2.13	1.91
80	1.4309	0.51	1.475	1.41
90	1.4411	0.51	0.87	0.86
100	1.4507	0.52	—	—

Maximum contraction was observed at tetrahydrofurfuryl alcohol contents of 40 to 60%, and contraction was consistently greater at 20° C. than at the higher temperature.

Tetrahydrofurfuryl alcohol has a considerably lower heat capacity, surface tension, and flash point than ethylene glycol (Table III). The specific heat

TABLE III

SPECIFIC HEAT, SURFACE TENSION, FLASH POINT, AND THERMAL EXPANSION VALUES FOR
TETRAHYDROFURFURYL ALCOHOL AND ETHYLENE GLYCOL

	Specific heat, 20°–27° C.	Surface tension, dynes/cm. at 25° C.	Flash point, ° C.	Thermal expansion, 20°–151.7° C. $\alpha \times 10^{-3}$
T.H.F.A.	0.424	37	85	0.747
Ethylene glycol	0.52	50.5	116	0.762

increases only slightly with rising temperature: 20° to 27° C., 0.424; 30° to 37° C., 0.432; 40° to 47° C., 0.445. The thermal expansion coefficient of tetrahydrofurfuryl alcohol corresponds closely to that of ethylene glycol. Observed D_4^t values for tetrahydrofurfuryl alcohol were 151.7° C., 0.964; 100°, 1.014; 37.8°, 1.049; 20°, 1.059.

The data of Table IV show that tetrahydrofurfuryl alcohol and ethylene glycol differ considerably in their action on natural and synthetic rubbers and that rubber compounds also vary in their resistance to the weakening

TABLE IV

EFFECTS OF ANHYDROUS ETHYLENE GLYCOL AND TETRAHYDROFURFURYL ALCOHOL ON NATURAL AND SYNTHETIC RUBBER COMPOUNDS

Criteria	Rubber	Untreated	Ethylene glycol	T.H.F.A.
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72 hr. immersion at 80° C.

Volume increase, %	Natural	—	0.6	10.9
	Buna S	—	1.5	22.2
	Neoprene	—	6.0	140.4
Tensile strength, lb./sq. in.	Natural	2955	2815	2720
	Buna S	3005	1540	1125
	Neoprene	2625	2340	975
Elongation at break, %	Natural	615	505	655
	Buna S	620	285	340
	Neoprene	840	640	750
Hardness, Type A, Shore	Natural	53	53	46
	Buna S	55	53	48
	Neoprene	54	51	12

50 hr. immersion at 154° C.

Volume increase, %	Natural	—	1.5	48.3
	Buna S	—	3.6	60.9
	Neoprene	—	39.4	251
Tensile strength, lb./sq. in.	Natural	2955	2460	995
	Buna S	3005	1550	815
	Neoprene	2625	1075	310
Elongation at break, %	Natural	615	585	805
	Buna S	620	275	445
	Neoprene	840	395	570
Hardness, Type A, Shore	Natural	53	47	16
	Buna S	55	55	32
	Neoprene	54	49	16

and softening effects of these liquids. Tetrahydrofurfuryl alcohol invariably caused greater swelling and softening, and a greater decrease in tensile strength. The 'elongation at break' for natural rubber was increased by tetrahydrofurfuryl alcohol and decreased by ethylene glycol. Elongation at break for Buna S and Neoprene was reduced by both liquids, and to a greater extent by ethylene glycol than by tetrahydrofurfuryl alcohol. Decreases in tensile strength and hardness were much greater at 154° C. than at 80° C.

All three rubber compounds were softened by exposure to tetrahydrofurfuryl alcohol at 154° C., and Neoprene was also seriously softened by tetrahydrofurfuryl alcohol at 80° C.

Table V reports effects of immersing radiator hose connections in 80% tetrahydrofurfuryl alcohol - 20% water and 60% ethylene glycol - 40% water solutions for 30 days at 80° to 82° C. As the liquids could enter the fabric at

TABLE V

EFFECT OF 60% ETHYLENE GLYCOL AND 80% TETRAHYDROFURFURYL ALCOHOL ON RADIATOR HOSE CONNECTIONS (30 DAYS' IMMERSION AT 81° C.)

Hose property	Hose No.	Untreated	60% ethylene glycol	80% T.H.F.A.
Inner hose diameter	1	1.50	1.45	1.45
	2	1.25	1.24	1.25
	3	1.68	1.55	1.59
	4	0.625	0.56	0.56
Adhesion of tube to fabric, lb./in.	1	7.0	6.0	4.2
	2	12.3	12.1	8.4
	3	11.3	8.8	6.5
	4	5.0	5.0	2.2
Hardness, Type A, Shore	1	87	79	59
	2	76	77	61
	3	86	57	51
	4	79	61	46
Volume increase, %	1	—	10.5	18.0
	2	—	6.7	23.2
	3	—	45.0	17.4
	4	—	14.2	15.8
Weight increase, %	1	—	8.3	13.6
	2	—	4.6	15.0
	3	—	30.6	11.2
	4	—	11.6	13.3

the cut ends of the tubes, the conditions in this respect were more severe than in a cooling system. Decreases in hose diameter were slight with both liquids. Adhesion of rubber to fabric was weakened and the samples were softened to a greater extent by the tetrahydrofurfuryl alcohol than by the ethylene glycol solution. Increase in hose weight and in volume also was greater with three out of four hose samples after immersion in tetrahydrofurfuryl alcohol.

The effects of the above coolants on radiator hose connections were compared further by the physical testing of hose removed from vehicles after a five month driving test. Hardness, tensile strength, adhesion, and internal diameters of the radiator hose were decreased about equally by this lengthy exposure to 80% tetrahydrofurfuryl alcohol and 60% ethylene glycol. The results indicate that tetrahydrofurfuryl alcohol has lesser effects in actual service than in laboratory immersion tests, and that its use would not seriously affect the serviceable life of hose connections. Important differences in

serviceability between individual hose connections may be anticipated, regardless of the coolant that is employed. After extensive tests on radiator hose exposed to a number of antifreeze solutions, Green *et al.* (11) concluded that the nature of the hose was of greater importance than the circulating fluid.

Metallic corrosion by aqueous tetrahydrofurfuryl alcohol solutions in the presence of inhibitors (0.1% sodium nitrite, 0.3% sodium chromate, 1% 'Tri Rad' emulsion) was subjected to preliminary study by two month immersion tests on bolted metal plates. Corrosion of steel, copper, brass, and aluminum was almost negligible in the presence of any one of the above inhibitors. Corrosion of lead and solder was serious in all tests with tetrahydrofurfuryl alcohol solutions, pure tetrahydrofurfuryl alcohol, and with ethylene glycol and other antifreeze solutions. Corrosion of the above metals was reduced to the level of insignificance in preliminary tests with an improved inhibitor formula, which was developed by the staff of the corrosion laboratory, and on which work is being continued.

Driving tests with tetrahydrofurfuryl alcohol thus far have been limited to the use of 80% tetrahydrofurfuryl alcohol - 20% water in the vicinity of Ottawa. During a five month test that was extended to midsummer, additional liquid was not required to correct evaporative and other losses. The tetrahydrofurfuryl alcohol solution that was finally drained off was more strongly colored and contained more sediment than 60% ethylene glycol after the same period of service. The effects of these liquids on the hose connections has already been discussed. With respect to engine performance and temperature, creeping, leakage, and odor, no differences were observed between motors cooled by glycol or by tetrahydrofurfuryl alcohol.

Discussion

The principal advantage of tetrahydrofurfuryl alcohol over other permanent type organic antifreeze solutions is low freezing point and viscosity at low water contents. Pure tetrahydrofurfuryl alcohol is less viscous than 60% ethylene glycol - 40% water at low temperatures and remains quite mobile at -70°C . (-100°F). The value of this property depends largely on the importance of protection beyond the liquid range of glycol-water mixtures. The low specific heat of tetrahydrofurfuryl alcohol and its deteriorative effects on rubber are unfavorable characteristics of the anhydrous liquid. Tetrahydrofurfuryl alcohol is judged almost equivalent to ethylene glycol with respect to stability, permanence, thermal expansion, inflammability, surface tension, and corrosiveness; the differences in these respects at least are not serious.

No advantage is foreseen for the use of tetrahydrofurfuryl alcohol as a freezing point depressant for water at the concentrations employed with other antifreeze compounds. With substantial reduction in price, a considerable market for this antifreeze might be found in regions of moderate climate. A

demand for nonvolatile antifreeze compounds of extremely low freezing point may be anticipated for use in northern Canada and Alaska, and for this application tetrahydrofurfuryl alcohol appears to warrant further attention.

Acknowledgments

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LIQUID AND FROZEN EGG

IV. REPRODUCIBILITY OF MEASUREMENTS OF REDUCING SUGAR IN FROZEN EGG¹

By J. W. HOPKINS² AND RUTH M. TREVOY²

Abstract

Analysis of 16 test samples in three collaborating laboratories indicated the desirability of initial standardization and periodic checking of reagents and of both sampling and analytical technique to ensure consistency of routine results. Average glucose content of a carlot of 1250 38-lb. containers might be determined with a standard error of the order of ± 10 mgm. per 100 gm. egg by a single analysis of each of two independent composite samples each obtained by combining and thoroughly mixing single 'cores' taken from 15 randomly chosen containers. This would also enable a running check to be kept on both the average and variance of the reported glucose contents by, e.g., 'control chart' methods. Precision of test results would be improved most effectively by increasing the number of individual containers sampled rather than the number of chemical analyses.

Object and Methods

Considerable quantities (amounting in 1947 to some 20,000,000 lb.) of eggs accumulated during the season of peak Canadian production are commercially preserved for use in the bakery and other trades by removing them from the shell, mixing yolks and whites, and freezing the resultant mixture in bulk containers holding 36 to 40 lb. Objective criteria for assessment of the quality of this frozen product are desirable, and it has been suggested (6) that reducing sugar content might be one such criterion, measurable in either plant or local consulting laboratories. Reproducibility within and between laboratories of this measurement has accordingly been studied with the results now described. Three Ottawa laboratories collaborated in the investigation. These were located in the Division of Chemistry, Science Service, Department of Agriculture (J. T. Janson); Food and Drug Division, Department of National Health and Welfare (L. I. Pugsley); and Division of Applied Biology, National Research Laboratories (J. A. Pearce). Test material consisted of 16 38-lb. pails of commercial frozen egg drawn from current production of plants in Montreal, Toronto, Ottawa, and Winnipeg. These will hereafter be designated by the letters A to P, while the collaborating laboratories will be denoted by the numbers 1, 2, and 3, which were allotted to them at random.

Fig. 1 illustrates schematically the procedure followed in apportioning and subsampling the test material. Apportioning was done in the National Research Laboratories. The contents of each pail was first divided into six $6\frac{1}{2}$ lb. portions by vertical slicing along equidistant radii of the top surface.

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² Biometrician.

The resulting portions were then kept in -40°F . storage pending distribution to the collaborators as scheduled in Table I. It may be observed from this schedule that the test extended over 16 working days, each laboratory receiving two of the above-mentioned $6\frac{1}{2}$ lb. portions, identified only by code number, for subsampling and analysis on each day. The schedule for each laboratory

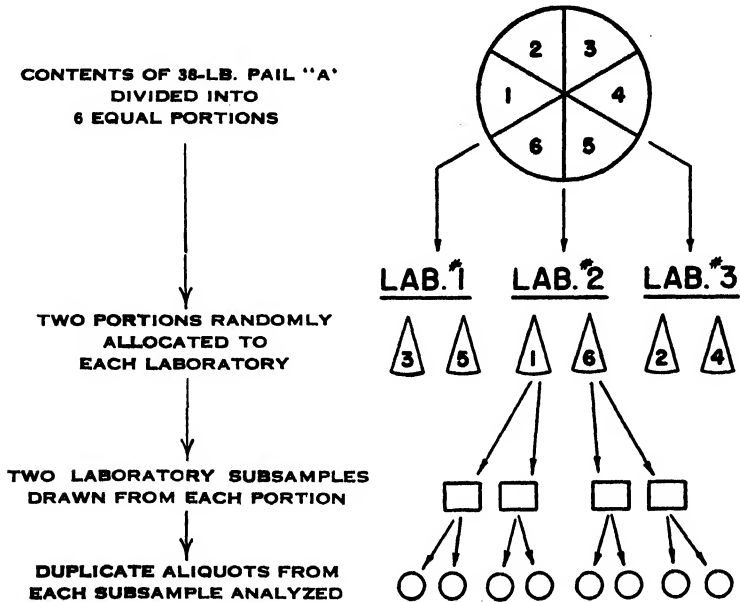


FIG. 1. Schematic representation of apportionment and subsampling of test material.

TABLE I
SCHEDULE OF DISTRIBUTION OF TEST PORTIONS

Day of test	Test material (designation A-P)					
	Laboratory 1		Laboratory 2		Laboratory 3	
	First	Second	First	Second	First	Second
1	B	P	E	H	M	F
2	N	K	G	M	C	A
3	F	O	N	B	P	O
4	J	G	P	A	E	B
5	A	M	F	C	L	J
6	P	B	H	E	F	M
7	C	E	O	K	I	D
8	I	H	L	I	H	K
9	G	J	A	P	B	E
10	M	A	C	F	J	L
11	L	D	D	J	N	N
12	D	L	J	D	G	G
13	E	C	K	O	N	I
14	K	N	M	G	D	C
15	O	F	B	N	A	P
16	H	I	I	L	K	H

was balanced in two respects. Firstly, over the 16-day period as a whole, one portion from every pail was analyzed as a 'first' and one as a 'second' daily sample, thus facilitating the detection of any consistent diurnal trend in results. Secondly, portions from eight pairs of pails were analyzed on two different days in each laboratory (e.g., from N and K on the second day and from K and N on the fourteenth day in Laboratory 1), so that marked differences between days affecting any or all laboratories might likewise be distinguishable from the inter-portion sampling variance. Apart from these limitations however, the order of distribution of the various portions was determined entirely from tables of random numbers (4).

From each submitted portion, the laboratories withdrew two independent small subsamples, which were carried through all further stages separately but concurrently. After the removal of protein in the manner specified by Folin and Wu (5, p. 416), the reducing sugar in 2 gm. of defrosted material was measured by the Shaffer-Hartmann titration procedure (5, pp. 437-438) and expressed as mgm. glucose per 100 gm. egg. Duplicate aliquots were titrated. All determinations in any one laboratory were made by a single technician in accordance with standardized instructions covering 21 specific items of procedure.

Results

Intra-laboratory Variance

The test provided information respecting the variability within each laboratory of aliquots from the same subsample, of subsamples from the same portion, and of portions from the same pail. This was examined statistically by Fisher's analysis of variance procedure (3).

Variance between duplicate aliquots from the same subsample, estimated from 64 comparison-pairs in each laboratory, differed as shown in Table II.

TABLE II
ESTIMATED INTRA-LABORATORY STANDARD DEVIATIONS

(Mgm. glucose per 100 gm. egg)

Source of variance	Standard deviation, mgm.		
	Lab. 1	Lab. 2	Lab. 3
Aliquots	5	2	11
Subsamples	19	9	9
Test portions	16	16	16

In Laboratory 1 it gave rise to a standard deviation of ± 5 mgm., this being $\pm 1.4\%$ of the average of 356 mgm. glucose per 100 gm. egg reported there for the test as a whole. In Laboratory 2 the aliquot standard deviation was ± 2 mgm., which was $\pm 0.6\%$ of this laboratory's average of 354 mgm.,

while in Laboratory 3 it was ± 11 , amounting to $\pm 3.5\%$ of the average of 319 mgm. The recorded aliquot standard deviation of Laboratory 2 was thus less than half, while that of Laboratory 3 was more than double, that of Laboratory 1.

Subsamples drawn from the same portion, on the other hand, were substantially less variable in both Laboratories 2 and 3 than in Laboratory 1. After allowing for the variance in aliquots described above, subsampling was estimated (1, 2), from 32 comparison-pairs in each instance, to have given rise to a standard deviation of ± 19 in Laboratory 1, but of only ± 9 mgm. in Laboratories 2 and 3.

As the test portions resulting from the initial division of the contents of each pail were allocated in an objectively random manner, variability in the results of all three collaborators due to any heterogeneity of such portions should have been of the same order. This was in fact the case. The net variance between portions after allowing for that in aliquots and in subsamples deduced above, estimated from 16 comparison-pairs in each laboratory, corresponded to a standard deviation of ± 16 mgm. glucose per 100 gm. egg. These differences in the results for portions from the same pail were apparently entirely random in character, no consistent discrepancy in average or variance between days, or between first and second sets of determinations made on the same day being detectable when the laboratories were considered either individually or collectively.

Inter-laboratory Variance

Table III and Fig. 2 provide a comparison of the results reported by the three collaborators. Each value listed is an average of two aliquots from two subsamples from two portions from each test pail, viz., of eight titrations in all. The concentration of experimental material in the upper part of the range of variation was presumably representative of current production but was not ideal for correlation studies. Agreement between Laboratories 1 and 2 appeared to be basically good, the individual and collective departures from equality, represented graphically by the distance of the hollow circles from the broken diagonal line in Fig. 2, being no more than the expectation computed from the previously estimated variance of test portions, subsamples, and aliquots. Laboratory 3's results on the other hand were in the aggregate significantly lower, and there was some suggestion that this discrepancy widened as the glucose content of the test material increased, corresponding pail averages for Laboratories 1 (x_1) and 3 (x_3) being related by the conversion equation (7)

$$x_3 = 100.1 + 0.616x_1$$

illustrated by the continuous line in Fig. 2. In the absence of additional results for the range 200 to 300 mgm., however, this may be subject to considerable revision, the standard error of the factor 0.616 being of the order of ± 0.15 .

TABLE III
TEST RESULTS REPORTED BY COLLABORATORS

Test material	Average reducing sugar reported (as mgm. glucose per 100 gm. egg)		
	Laboratory 1	Laboratory 2	Laboratory 3
A	381	381	318
B	336	373	333
C	376	372	297
D	197	212	216
E	349	306	296
F	368	343	357
G	363	359	333
H	383	341	300
I	382	356	319
J	367	378	329
K	351	345	323
L	337	358	357
M	354	357	339
N	377	387	330
O	411	396	331
P	358	404	329
Average	356	354	319

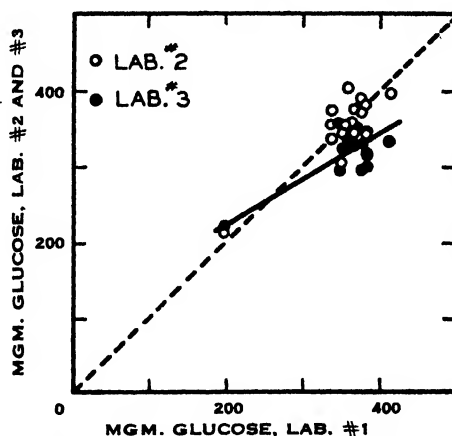


FIG. 2. Graphical comparison of glucose contents of 16 test materials reported by three collaborating laboratories.

Conclusions

If current stocks were to be tested, practical considerations would require estimation of the average reducing sugar content of carload shipments of 1250 or more pails from single core samples taken from about 2% and amalgamated to form composites for analysis in local consulting laboratories. Subsequent comments relate to these imposed conditions.

The foregoing experiment of course strongly suggests that initial standardization, and periodic checking, of reagents and of both sampling and analytical technique would be desirable to ensure consistency of grading in all localities.

The over-all standard deviation of results for carlots obtained as outlined would reflect inter-pail as well as intra-pail variability. The 16 pails A-P considered above were characterized by a net variance (after allowing for sampling, subsampling and aliquot fluctuations) of 1882, corresponding to a standard deviation of ± 43 mgm. glucose per 100 gm. egg. This figure may exceed the actual variability within carlots from a single plant, but makes possible an approximate estimation of the level of precision likely to be attained in practice. If the variance of inter- and intra-pail sampling, of laboratory subsampling, and of individual aliquots be denoted by v_1 , v_2 , v_3 , and v_4 , and if it be supposed (a) that a carlot comprises 1250 pails of which a random 2.4% are subjected to single-core sampling; (b) that the resulting 30 cores are combined to form two thoroughly mixed 15-core composites for independent analysis; (c) that from each of these composites a laboratory subcomposite is formed by withdrawing and again thoroughly mixing three independent laboratory subsamples; and (d) that one chemical determination is made on a 2 gm. portion of each such subcomposite: then the standard error to be expected in the average of the two determinations thus made on material from each carlot would be

$$\pm [(v_1 + v_2)/30 + v_3/6 + v_4/2]^{\frac{1}{2}}.$$

With $v_1 = 1882$ as above, $v_2 = 249$ as in the average for Laboratories 1, 2, and 3, $v_3 = 77$ as in Laboratories 1 and 2 and $v_4 = 29$ as in Laboratory 1, this would amount to roughly

$$\pm (63 + 8 + 13 + 15)^{\frac{1}{2}},$$

i.e., of the order of ± 10 mgm. per 100 gm. egg. Hence, if for example a grade specification of not less than 300 mgm. per 100 gm. were established and shipments were inspected in the above way, a carlot for which the average was actually 275 mgm. or lower should have less than 1 chance in 100 of being accepted, while one for which the true average was 325 mgm. or higher should stand less than 1 chance in 100 of being degraded. The indications are that this margin of buyer's and seller's risk would be most effectively reduced by increasing the proportion of pails sampled rather than the number of laboratory analyses.

Of course, this estimate of likely precision must be regarded as tentative, as its major component, inter-pail variance, is only approximately known. However, in the event of the procedure being adopted for routine grading, analysis of two independent core-composites from each carlot would soon provide more definite information on this point, as well as enabling a running check to be kept on both the average and variance of the reported glucose contents by 'control chart' or other methods (8). Duplicate analyses would permit a similar running check to be kept on laboratory technique, but would add to laboratory costs without effecting a corresponding increase in the over-all precision of the results.

Acknowledgments

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THE OXIDATION, IGNITION, AND DETONATION OF FUEL VAPORS AND GASES

IV. THE CAUSE OF DETONATION OR COMBUSTION KNOCK IN ENGINES¹

BY R. O. KING²

Abstract

A nuclear theory of self-ignition is described which is based on the substitution of finely divided carbon for the nuclear drops of the Callendar theory. The finely divided carbon appears in the gaseous combustible mixture in the engine as a result of pyrolysis of the lubricating oil or of the fuel. The theory is therefore of general application and can be applied to explain combustion knock or detonation when permanent gases such as hydrogen as well as hydrocarbon vapors are used as fuel for the carburetor type of internal combustion engine. The theory is supported by experimental evidence quoted mainly from earlier publications and is intended as a working hypothesis for further confirmatory experiments.

Introduction

The experiments described in preceding Parts were directed mainly to ascertain the cause of the effect of metallic dopes to delay the onset of detonation in engines. They support the view that delay or prevention is due to dilution of the end gas by the products, steam and carbon dioxide, of an oxidation reaction occurring on the surface of the combustion space made 'active' by metal deposited on the thermal decomposition of the dope. The detonation delaying effect of dilution would operate whatever the cause of detonation, and discussion of that effect was therefore withheld pending a description of especially related experiments. Some of the experiments have been completed and others are in progress. It is hoped to describe all of them in succeeding Parts. It will, however, be of assistance to the reader and save space later if the working hypothesis used to plan the experimental work is given separately in this Part after a brief review of recent theory.

Section I

The Callendar Nuclear Theory of Self Ignition

The continued propagation of flame in a combustible mixture after ignition at a point depends, according to the classical theory, on the rate of heat generation by combustion continuing to be greater than the rate of loss by conduction, convection, and radiation. The theory does not provide an adequate explanation for the sudden increase in flame velocity in a tube after a certain distance has been traversed by the flame front or the similar effect in the combustion space of an engine. In fact, ignition of the unburned gas well ahead of the flame front, that is, self-ignition, can be obtained in

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suitable conditions of temperature and pressure. Self-ignition of the end gas in an engine results in detonation, indicated by combustion knock which occurs also if the rate of flame propagation become abnormally great.

A nuclear theory of self-ignition was advanced by Callendar (7, 8) to explain the occurrence of detonation in an engine and the antiknock effect of metallic dopes. In the particular case of ordinary liquid hydrocarbon fuels, always containing some proportion of high boiling point constituents, it was considered that the nuclei would be liquid drops of the higher boiling point fractions remaining after evaporation of the lighter fractions of the fuel. These residual drops, as they evaporate, would be contained within a shell of nearly pure vapor which would recondense in part as the compression pressure was raised because hydrocarbon vapor, unlike steam, tends to condense on compression. Vaporization would thus be retarded and the drops could persist until late in the period of combustion. The drops, being surrounded by vapor of the high boiling point constituents of the fuel, would have a lower ignition temperature than that of the gaseous mixture in which they were dispersed. Thus if the end gas were impregnated with liquid drops, nearly simultaneous ignition (detonation) might occur prior to the completion of combustion of the gas in the normal course of flame travel.

Hydrocarbon fuels completely vaporized and mixed with air in combining proportions present some difficulties because condensation during compression could not occur in the circumstances. Callendar suggested that in such cases the smoke particles which are always present in the operation of an internal combustion engine would serve as foci of condensation and "with the aid of such carbon nuclei, drops of a highly ignitable nature may continue to exist or *may be formed by condensation* at temperatures such that the mixture should be completely vaporized according to the ordinary rules of calculation."

The possibility that carbon nuclei as such might be effective centers of ignition in an otherwise homogeneous gaseous combustible mixture was not discussed. The carbon nuclei mentioned as being present in the engine combustion space were the smoke particles remaining from the previous combustion of hydrocarbons, and it was suggested only that they could promote the *formation of liquid drops* in a completely vaporized mixture by serving as foci of condensation.

Aside from the failure of the nuclear drop theory to account for detonation in completely vaporized mixtures, there appeared to be some doubt about the drops being present in sufficient concentration in the end gas to provide an igniting effect, and Callendar's suggestion that the metallic dope prevented ignition of the drops by plating them with metal, thus preventing absorption of radiation from the flame, was not convincing. The chemical side of the problem was therefore explored at his request but with the fixed idea that some product of the oxidation of the rich mixture surrounding the slowly evaporating drops would be readily inflammable and thus ignite the drops.

Oxidation, according to the Armstrong-Bone hydroxylation theory, then generally accepted, would begin with the formation of an alcohol and proceed by further oxidation to aldehyde, carbon monoxide, steam, and carbon dioxide. All the oxidation products mentioned, except the aldehyde, were known to delay detonation. A number of aldehydes were tried as additions to engine fuel but proved to be of inappreciable effect on detonation (5, p. 183; 6, p. 20). The idea that detonation must be due to the accumulation of some oxidation product in the nuclear drops was however not abandoned. It was known that certain unstable organic peroxides decomposed with some violence on heating, and it was suggested (by Mardles) that a peroxide instead of an alcohol might be the primary oxidation product. The suggestion fitted exceptionally well into the nuclear drop theory, and, as the result of numerous confirmatory experiments, Callendar concluded (5, 6), in respect of *paraffinic fuels and ether*, that although the amount of peroxide formed would not in itself be sufficient to cause the detonation observed it would act as a primer for the simultaneous ignition of the nuclear drops—and detonation thus caused would be prevented if metallic dope were concentrated in the drops owing to the reduction of the peroxide by the metal of the dope.

It will be noted that the nuclear theory remained encumbered by liquid drops and, although it could not be accepted as having more than a limited field of application, the idea that organic peroxides were responsible in some way for fuel detonation in engines received fairly general approval in large part because it seemed to pave the way for the application of chain reaction theories to combustion as it occurs in the engine.

Section II

Chain Reaction Theory

A nonhomogeneous combustible mixture is a necessary prelude to self-ignition, according to the nuclear theory. The chain reaction theory was devised to account for oxidation leading to ignition in a homogeneous mixture, reaction being between single molecules. Experimental evidence in support of the theory has been generally obtained by using reacting mixtures not diluted with nitrogen, at relatively low pressures and without taking flow configuration (15) into account. Nevertheless many attempts have been made to use the theory to explain the mechanism of oxidation and detonation in the turbulent fuel-air mixtures used in engines at the extremely high pressures attained during combustion of the end gas, although mixtures so diluted with nitrogen cannot be detonated in tubes.

There is little agreement about the manner of initiation of chain reactions and still less about the mechanism of the reaction. It is most simple to suppose, as suggested by Mardles (5, 6) and by Moureu, Dufraisse, and Chaux (18), that a collision between a fuel and an oxygen molecule results in the formation of a peroxide having a relatively high energy content, and Egerton (9) considers that reactivity is handed on from the peroxide to new reactant

molecules, the reaction being autocatalytic in character, a view that is not in accordance with the Armstrong-Bone hydroxylation theory in support of which there is considerable experimental evidence if reaction occur at high pressure. Egerton considers that the metallic antiknocks delay oxidation by forming metallic peroxides that react with and destroy the fuel peroxides, thus breaking the reaction chains and preventing detonation.

Norrish (19) considers the peroxidation theory to be unsatisfactory and suggests that reaction chains start from the aldehyde and proceed by an "atomic chain" mechanism according to which methane for example would be oxidized by a chain reaction involving free radicals and atomic carbon. Oxidation of other hydrocarbons requires atomic oxygen as a link in the chain reaction. Norrish, to a considerable extent, avoids conflict with the hydroxylation theory of oxidation but does not, in the reference given, apply his chain reaction theory to explain the action of metallic antiknocks.

Rice (21) considers that thermal decomposition results in the replacement of one molecule of hydrocarbon by several, with the result that the increase in concentration may greatly augment rate of oxidation and increase knocking tendency accordingly, oxidation being a chain reaction involving free radicals. Metallic antiknocks are assumed to cause the fuel molecule to decompose into relatively few small molecules and in this way reduce knock. Rice appears to envisage a limited decomposition, unlike Norrish who assumes decomposition to carbon or oxygen atoms.

Steele (23) suggests that hydrogen liberated by the decomposition of hydrocarbons during the combustion period in the engine is responsible for fuel knock. He considers this view to be supported by the engine experiments of A. F. Burstall showing that hydrogen gives rise to violent knock (4) while carbon monoxide does not knock in any circumstances (3). It is further suggested by Steele that the knock due to hydrogen liberated by decomposition of the hydrocarbon can be prevented by adding more hydrogen to carry the partial pressure out of "a critical range."

Boerlage and Van Dyck (1) established a relation between the *initial* cracking speeds of Diesel engine fuels and the cetene numbers with a considerable degree of success. An attempt to establish a relation between the *initial* cracking speeds of fuels used with carburetor engines and octane numbers was less successful. The initial cracking speed of iso-octane which is at the top of the octane scale was, for example, greater than that of heptane which is at the bottom of the scale. The initial cracking speed of heptane was however greater than that of some hydrocarbons of a higher octane rating. The experiments were made at atmospheric pressure and conditions were not the most suitable for cracking the hydrocarbons to carbon. The experimenters assumed that detonation depends on a high rate of oxidation in a homogeneous mixture of hydrocarbon vapor and air, and were most concerned with the gaseous products of cracking in an endeavor to determine the conditions in which free radicals or an active form of oxygen would be present and initiate chain reactions.

The above brief review of chain reaction theory as applied to combustion in the engine is admittedly superficial. It has been given to illustrate in some degree the difficulties met with in applying the theory to explain the cause of detonation in an engine and the action of antiknocks. The metallic antiknocks decompose at temperatures reached before the end of compression and the metal, which is generally agreed to be the active agent to prevent knock, is deposited mainly on surfaces. It is difficult to understand how this metal can be present later on to break reaction chains in the end gas. Similarly it is difficult to understand how organic peroxides, which by definition are initial and unstable products of slow oxidation at relatively low temperatures, can persist and be essential links in chain reactions occurring at the extremely high temperatures of the end gas. The Callendar nuclear drop theory did at least provide a means of their persistence. Finally, Egerton in a lengthy discussion of "Existing knowledge on knocking and its prevention" (10), states "although it would be generally agreed that in the oxidation of saturated paraffins, reaction chains are operative, there is as yet no agreement on the mechanism of the process or the nature of the chain carriers."

Section III

Heterogeneous Oxidation Reactions and a Revised Nuclear Theory of Self-Ignition

Outline of Theory

The experiments described in preceding Parts indicate that flameless oxidation of fuel in mixtures with air in engine conditions occurs solely on hot surfaces, not in the body of the gas by a chain reaction process. The surfaces in the combustion space of an engine may comprise areas of metal, metallic oxides, adherent carbonaceous matter, or carbon distributed in the combustible mixture as fine particles. When the surfaces reach a suitable temperature oxidation may be to partial or final products in accordance with the nature of the surfaces and the degree of turbulence. The heat of reaction does not suffice to start a flame if surface temperature is controlled by water or air cooling, and combustion after spark ignition proceeds to completion without the occurrence of pre-ignition or detonation. It is to be noted that the temperature of containing surfaces can be controlled but not that of the surfaces of material nuclei in the body of the gas.

Flame may, however, be started without spark ignition if a surface become so thickly coated with carbon that external cooling is ineffective or if insufficiently cooled points or small areas become incandescent. Flame may also be started by the combustion of aldehydes which are formed in great profusion in conditions of excessive turbulence, and can be ignited by contact with surfaces at the temperature attained in high duty engines by the exhaust valve. Thus methyl and ethyl alcohols, which oxidize in the first stage to aldehydes, are especially prone to pre-ignition when used as engine fuel for the Ricardo E35 engine in spite of the cooling effect arising from the high latent heat of evaporation.

Flame started in any of the ways mentioned moves through the combustible mixture just as if it had been started by an electric spark and does not give rise to detonation. If the flame starts before the passage of the spark it is described as pre-ignition and if timing is approximately correct the engine will run without spark ignition.

Detonation as it occurs in an engine using hydrocarbon fuel can be initiated solely if flame be started nearly simultaneously at points distributed throughout the end gas, and experiments indicate that the conditions required are governed by the temperature and pressure of the gas and the concentration in it of carbon nuclei, the concentration being determined, other things being equal, by the pressure. The theory will now be discussed in greater detail.

End Gas Temperature and Pressure

The temperatures and pressures attained by the end gas at compression ratios extending from 4 to 10 : 1 given in Table I below are calculated on the basis that detonation occurs when the combustion pressure reaches 90% of the maximum value.

TABLE I

END GAS TEMPERATURES AND PRESSURES, RICARDO E35 VARIABLE COMPRESSION ENGINE

Compression ratio	Initial compression pressure	Initial compression temperature, ° C.	90% of max. combustion pressure, lb./sq. in.	Calculated temperature of end gas, ° C.
4 : 1	Atmospheric	133	346	673
5 : 1	"	112	477	707
6 : 1	"	102	616	741
7 : 1	"	95	—	765
8 : 1	"	90	—	809
10 : 1	"	—	—	877

The data used to compile the table are from published performance figures in respect of the Ricardo E35 variable compression engine (5, p. 211; 6, p. 26; 20). The end gas temperatures were calculated taking the value of γ to be 1.36. This allows for the end gas receiving some heat during the combustion period. If the temperature at the end of compression by the piston were required, the value of γ would be taken to be 1.34. The end gas temperatures for compression ratios of 7 to 10 : 1 are extrapolated values, indicator diagrams not being available. It will be noted that end gas temperature is very nearly a linear function of compression ratio, and, evaluating the constants, — end gas temp. = $(34 \times \text{C.R.} + 537)^\circ \text{C}$.

Nuclear Ignition

The Callendar theory of self-ignition was based on the nuclei, dispersed in a combustible gaseous mixture, having a lower ignition temperature than the otherwise homogeneous gas (7, 8). It was, however, shown by the later experiments of King (16) and King and Mole (17) that the nuclei need not

be of a combustible substance. Fine drops of water, stone dust, or powdered metallic oxides are all effective explosion agents. A description of experiments showing the igniting effect of a variety of nuclei in respect of mixtures of hydrogen, ethylene, and methane is given in the references quoted. Similar igniting effects were obtained at the time, in respect of carbon monoxide and acetylene. Experiments made later, with the arrangement of apparatus described in the references, in the Colloid Science Department, Cambridge University, demonstrated that pentane-air mixtures were especially sensitive to ignition by nuclei. When the mixture was supplied to the combustion tube at the rate of 300 cc. per min. explosion occurred at $570^{\circ}\text{C}.$, but nuclei such as finely divided silica caused explosion at $450^{\circ}\text{C}.$ and the still lower explosion temperature of $350^{\circ}\text{C}.$ was observed when the nuclei were fine particles of nickel oxide. Carbon was found to be an effective igniting agent but the variety used was so finely divided that the particles tended to stick together and float about instead of falling rapidly through the heated mixture. The cause of the effect is still a subject of speculation but there are two possibilities, one chemical, the other electrical. A reasonable chemical explanation is that the nuclei provide surfaces in the gas on which oxidation can occur, with the consequence that the heat of reaction would raise the temperature sufficiently to start a flame. It is difficult to apply this explanation to a particle of water, which would be evaporated to steam in the process. An electrical explanation seems to apply better to drops of water. It is known that such drops become positively electrified when falling through air even at atmospheric temperatures, and the potential of the charge would increase as the surface area decreased as evaporation proceeded. It is not impossible that ignition is electrical in some cases and due to the heat of chemical reaction in others. However, considering combustible nuclei such as carbon particles which, as will be shown in a subsequent Part, are especially effective to ignite combustible gaseous mixtures, it is reasonable to suppose that flame is started by the heat of the oxidation reaction even if the hot carbon particles which are pyrophoric, are themselves insufficient. Thus, with reference to Table I, the temperature of the end gas late in the period of combustion in an engine exceeds $600^{\circ}\text{C}.$ even at the low compression ratio of 4 : 1. Carbon particles derived from cracking of hydrocarbon fuel would be red hot in the circumstances and tend to start a flame in most combustible mixtures even if temperature were not further increased by oxidation of the gas in contact with them and by radiation from the advancing flame. At the relatively high compression ratio of 6 : 1 temperature in the end gas exceeds $700^{\circ}\text{C}.$, Table I, and the carbon particles would be in an active state of combustion.

Carbon Formation in the Engine Combustion Space

Pyrolysis of the lubricating oil yields free carbon. The carbon may be contained in part in sticky substances tending to adhere to surfaces and in part as fine particles which appear in the exhaust when the lubricant passes the piston at an excessive rate. The extent of the formation of adherent

carbonaceous matter, rather than of free carbon distributed throughout the combustible gaseous mixture, depends on factors such as the natures of the lubricant and of the fuel as well as mixture strength. Free carbon derived from the lubricating oil would 'be distributed throughout the whole of the combustible mixture, not especially concentrated in the end gas. Detonation is therefore not attributed to ignition by such carbon nuclei. They may, however, act to increase rate of flame propagation.

A second source of free carbon is found in the cracking of fuel molecules in the flame front. Thus Haslam and Russell (14), referring to the combustion of hydrocarbons, state that "under ordinary combustion conditions there is a race between thermal decomposition or "cracking" and the process of hydroxylation (oxidation). If the conditions favor oxidation there will be no soot. On the other hand if the conditions favor cracking the hydrocarbon will decompose into carbon and hydrogen and will burn with a smoky flame." The conditions in the engine favor cracking. Thus the flame as it moves through the combustible mixture, impinges on relatively cool surfaces and the formation of soot would be expected. The conditions are in fact similar to those used to procure 'acetylene black' from the burning gas, and it is significant that although the molecule of acetylene is thermally stable at end gas temperatures when the gas is diluted with nitrogen (22), yet the gas cannot be used as engine fuel even at low compression ratios because of the violence of detonation. It may be concluded therefore that free carbon is carried into the end gas by the turbulence which always accompanies the movement of flame and provides the distributed ignition centers required for detonation.

The third source of free carbon, namely the cracking of the end gas, provides ignition nuclei just where required to promote detonation. There is however little information available in respect of the rate of carbon formation when pentane and other hydrocarbons usually present in fuel for carburetor engines are decomposed at the temperatures and pressures of the end gas as given in Table I. It was observed by Callendar and associates (5, 6) that the combustion of paraffins ranging from pentane to undecane was accompanied by a fine persistent fog, some of which passed through the train of absorption apparatus. Similar effects were observed during later experiments and quoting from notes made at the time and referring to the combustion of pentane "Both oxidation and decomposition became appreciable at 300° C. A feature is that decomposition is delayed if oxidation proceed rapidly but on the other hand a rapid rate of decomposition as indicated by the volume of smoke issuing from the combustion tube is a sure indication of a slow rate of oxidation." It appears therefore that the relation between hydrocarbon oxidation and decomposition reactions in flameless combustion is similar to that described by Haslam and Russell in respect of combustion in a flame, as already mentioned.

Furthermore it is well known in engine practice that a non-knocking 'correct' mixture burns with a nearly colorless flame and that it becomes white and luminous if detonation occur. Withrow and Rassweiler, for example, found it necessary to use a considerable proportion of benzene in the fuel mixture in order to obtain photographs of a non-knocking combustion or of the flame movement prior to knock.

Another matter of interest is the incandescent carbon appearing in bright patches mainly around the inlet valve, top left-hand corner of the pictures. It can be seen first in the picture taken at 14.2° after top dead center and continues to glow throughout subsequent pictures, remaining incandescent after combustion of the gaseous mixture is substantially complete.

It is also of interest to compare the explosion times in an engine combustion space with those observed by Fenning for explosions in a bomb (12). The bomb was cleaned between explosions by blowing out with air and there was of course no lubricating oil. There would therefore be no carbon nuclei in the combustible mixture at the time of ignition by the spark, and such nuclei as would be formed by pyrolysis of the hydrocarbon would not appear until late in the explosion period. In the circumstances the period of time between the passage of the spark and the attainment of maximum pressure when using a nearly 'correct' air-petrol mixture was 18 times that observed by Withrow and Rassweiler in the engine combustion experiments just described. Moreover Fenning did not obtain detonation until the mixture was made overrich in petrol, 10.7 to 1, air-petrol, a circumstance promoting the formation of carbon by pyrolysis in the mixture ahead of the flame. The explosion time could not then be observed because the indicator mirror was knocked off the pivots. However, in a 12.9 to 1 air-petrol mixture which just did not detonate, the explosion time was 0.0682 sec. as compared with the 0.0780 sec. observed when the mixture was nearly 'correct'.

The relatively long explosion time in a bomb is usually attributed to the degree of turbulence in the mixture being less than in engine conditions, but in the Withrow and Rassweiler experiments the engine speed was 900 r.p.m. only, the combustion space was not of a turbulent type, and the photographs do not show any mass movement of the burning mixture until late in the combustion period. The conclusion is that the extremely high rate of flame propagation in an engine is due in large part to the carbon nuclei necessarily present throughout the combustible mixture.

Conclusions

The revised nuclear theory of self-ignition, which substitutes carbon particles due to pyrolysis for the liquid drops of the Callendar theory, is complementary to the revised theory of surface oxidation developed in Parts I, II, and III to account for the effect of metallic antiknocks to delay or prevent detonation in carburetor engines using hydrocarbon fuels. Thus the

PLATE I

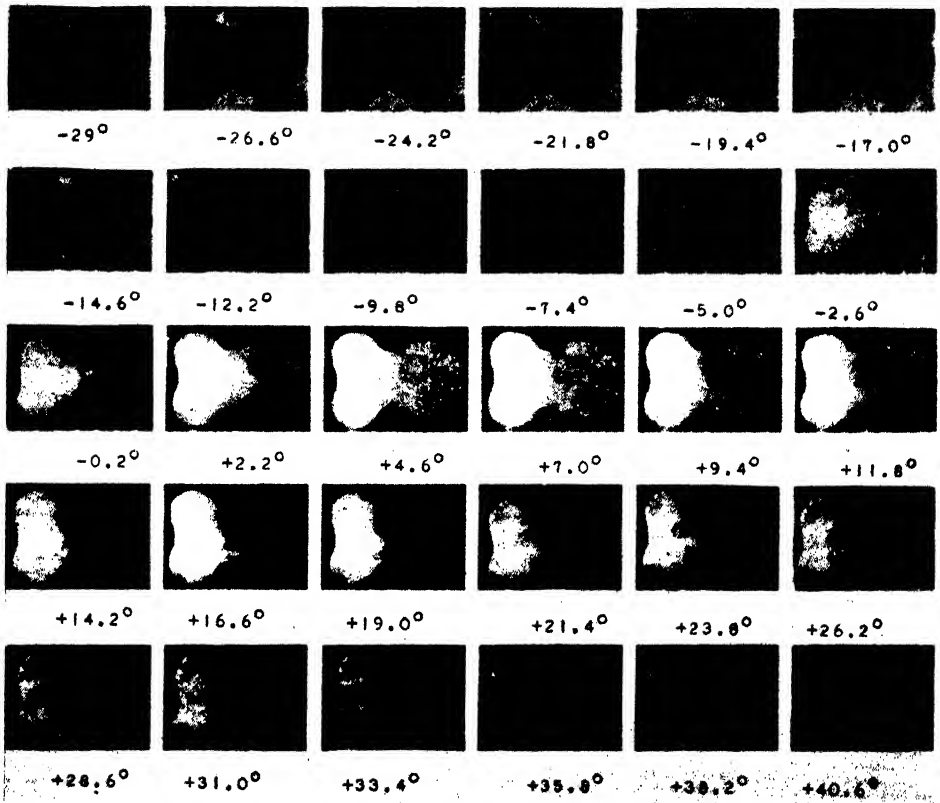


FIG. 1. Photographs of knocking combustion in an engine, taken by Withrow and Rassweiler over the period 29° before to 40.6° after top dead center at intervals of 2.4° of crank angle, engine speed 900 r.p.m.

unburned mixture ahead of the flame is subjected simultaneously to pyrolysis and to oxidation on the contact surfaces. The extent of the heterogeneous oxidation reaction and the nature of the products depends on the degree of turbulence in the mixture, the nature and temperatures of the surfaces, and the combustible mixture. The products of the reaction may be aldehyde, carbon oxides, and steam in varying proportions and are carried into the body of the end gas by turbulence and can be detected therein by chemical or spectroscopic methods of analysis. The end gas, diluted accordingly, tends to become noninflammable by finely divided carbon when the nature and temperature of contact surfaces are such that steam and carbon dioxide constitute a large proportion of the products of the heterogeneous reaction. That is, whether or not detonation occur in particular conditions depends on the result of a race between pyrolysis and a heterogeneous oxidation reaction. Detonation may be described in popular terms as differing from the familiar dust explosion solely in that the combustible dust is distributed in an ignitable mixture of air and gaseous fuel instead of in air only.

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THE VISCOSITIES AND DENSITIES OF CHLOROSULPHONIC ACID - SULPHUR TRIOXIDE MIXTURES¹

By K. J. McCALLUM AND E. L. TOLLEFSON²

Abstract

The viscosities and densities of crude chlorosulphonic acid - sulphur trioxide mixtures have been determined for compositions between 10 and 70%. The viscosity measurements were carried out at temperatures between 20° and -40° C. for those liquids that did not show crystallization over this range. At temperatures at which the complete range of compositions could be investigated, both the density- and viscosity-composition curves exhibit a maximum.

Introduction

No previous reports of measurements of the viscosity of mixtures of sulphur trioxide and chlorosulphonic acid appear in the published literature. The work reported here was undertaken to provide such data for this system. Since it was desired to obtain values applicable to commercial materials, all measurements were made on the commercial products without preliminary purification.

Apparatus, Experimental Procedure and Materials

All measurements were carried out in a constant temperature bath that consisted of a Dewar flask filled with gasoline and fitted with a toluene filled thermometer (calibrated against a platinum resistance thermometer), a stirrer, a thermoregulator, and a cooling coil. The thermoregulator controlled a small centrifugal pump that circulated gasoline through the cooling coil from an auxiliary cooling bath. The latter was cooled with dry ice to a temperature a few degrees below that desired in the constant temperature bath. With such an arrangement, it was observed that the temperature remained constant to $\pm 0.1^\circ$ C. in the temperature range from 20° to -40° C.

The viscosity measurements were made with two Ostwald type viscosimeters fitted with phosphorus pentoxide tubes to prevent absorption of atmospheric moisture by the very hygroscopic liquids that were under investigation. The flow of the liquid in the viscosimeter was observed from above by means of two small mirrors attached to the viscosimeter tube at an angle of 45°.

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The constants for these viscosimeters were obtained using two standard oils of known viscosity supplied by the United States Bureau of Standards.

The densities of the liquids were measured using a modification of the standard Sprengel specific gravity tube. It was furnished with an additional bulb blown in one of the side arms above the filling mark to allow for the expansion of the liquid as it warmed up from the low temperature at which the measurement was made to the temperature of the balance. To prevent absorption of water vapor from the atmosphere, the arms were equipped with ground-glass caps.

As the primary object of this work was to obtain viscosity data applicable to commercial products, all measurements were made on the crude materials, with no preliminary purification. The following materials were used in preparing the mixtures.

- (a) A mixture of chlorosulphonic acid and sulphur trioxide received from Suffield Experimental Station. Analysis by a method described later gave chlorosulphonic acid 45.51%, sulphur trioxide 54.25%, undetermined 0.24%.
- (b) Practical grade chlorosulphonic acid supplied by the Eastman Kodak Company.
- (c) Sulphur trioxide supplied by Suffield Experimental Station. When received it was in the form of a dark solid, which was melted before use.

Two series of mixtures were prepared, with compositions ranging from approximately 10% to 70% sulphur trioxide. Series *A* mixtures were prepared by the addition of either sulphur trioxide or chlorosulphonic acid to the commercial mixture, while Series *B* liquids were prepared by the direct addition of sulphur trioxide to chlorosulphonic acid.

The mixtures so prepared were analyzed by the following method. A small glass bulb was blown on a piece of glass tubing having a capillary tip. After weighing, the bulb was warmed slightly and the capillary tip was placed in the liquid to be analyzed. After some liquid had been drawn into the bulb, the capillary was sealed and the bulb and contents weighed, the increase in weight giving the weight of the sample. The filled sampling bulb was then placed in a 500 ml. glass stoppered Erlenmeyer flask containing a small amount of distilled water, and the bulb was broken by shaking. When the vapors formed had been absorbed by the water, the solution was titrated with standard sodium hydroxide solution, using phenolphthalein as the indicator. The end point of this titration having been reached, the sample was next titrated with standard silver nitrate solution using Fajan's method.

The weight of chlorosulphonic acid was calculated from the chloride analysis, and the weight of sulphur trioxide from the acidity not accounted for by the chlorosulphonic acid. The results of these analyses are given in Tables I and II.

Results and Discussion

The densities of the mixtures in Series *A* were measured at 20° and 0° C. while the Series *B* mixtures were measured at 20°, 0°, -10°, and -20° C. The results are given in Tables I and II, respectively. For the calculation of the viscosities, the values of the densities at other temperatures were obtained by assuming a linear relation between density and temperature over the range investigated.

TABLE I

COMPOSITION AND DENSITIES OF CHLOROSULPHONIC ACID - SULPHUR TRIOXIDE MIXTURES

Series *A*

Sample No.	Composition			Density, gm./cc.	
	% HSO ₃ Cl	% SO ₃	% Undetermined	0° C.	20° C.
A1	86.65	12.80	0.55	1.824	1.794
A2	76.65	23.06	0.48	1.865	1.834
A3	65.23	34.49	0.28	1.909	1.874
A4	55.04	44.43	0.53	1.943	1.906
A5	45.51	54.25	0.24	1.967	1.925
A6	36.88	62.77	0.35	1.981	1.932
A7	28.10	71.06	0.84	1.992	1.941

TABLE II

COMPOSITION AND DENSITIES OF CHLOROSULPHONIC ACID - SULPHUR TRIOXIDE MIXTURES

Series *B*

Sample No.	Composition			Density, gm./cc.			
	% HSO ₃ Cl	% SO ₃	% Un- determined	20° C.	0° C.	-10° C.	-20° C.
B1	89.15	10.92	—	1.783	1.813	1.827	1.843
B2	77.86	22.12	0.02	1.824	1.855	1.870	1.885
B3	67.83	31.87	0.30	1.860	1.891	1.906	1.924
B4	57.97	41.37	0.66	1.892	1.926	1.942	1.959
B5	48.50	51.09	0.41	1.917	1.955	1.973	1.990
B6	38.89	59.58	0.53	1.936	1.978	1.998	2.015
B7	31.36	68.45	0.19	1.943	1.989	2.013	—

The results of the viscosity measurements on the mixtures of Series *A* and Series *B* are given in Tables III and IV, respectively. The determinations were carried out at temperatures down to -40° C., unless crystallization occurred before this temperature was reached.

TABLE III
VISCOSITIES OF CHLOROSULPHONIC ACID - SULPHUR TRIOXIDE MIXTURES
Series A

Sample No.	Viscosity, millipoises			
	20° C.	0° C.	-20° C.	-40° C.
A1	46.8	77.1	147.9	385.7
A2	58.7	108.2	241.7	837.1
A3	83.6	177.4	479.8	2411.0
A4	108.8	274.4	952.6	7335.0
A5	120.8	344.4	1537.0	17360.0
A6	117.8	372.8	1931.0	—
A7	108.4	378.4	—	—

TABLE IV
VISCOSITIES OF CHLOROSULPHONIC ACID - SULPHUR TRIOXIDE MIXTURES
Series B

Sample No.	Viscosity, millipoises						
	20° C.	10° C.	0° C.	-10° C.	-20° C.	-30° C.	-40° C.
B1	39.3	48.8	62.7	85.4	117.3	176.2	294.1
B2	56.0	71.7	98.3	140.7	209.2	353.7	695.2
B3	81.9	103.8	149.9	233.5	384.2	735.3	1683.0
B4	104.8	155.0	239.8	410.7	775.1	1721.0	4881.0
B5	129.6	204.9	352.3	669.5	1401.0	3751.0	12710.0
B6	136.8	232.8	434.6	933.0	2302.0	7205.0	—
B7	121.8	216.8	425.4	—	—	—	—

Since the measurements on the Series *B* liquids were carried out over a wider temperature range than on those of Series *A*, only the former are presented in graphical form.

Fig. 1 shows the density of the Series *B* liquids as a function of the percentage of sulphur trioxide. Included in this plot are the densities of the pure components chlorosulphonic acid and sulphur trioxide at 20° C. as given in the International Critical Tables. In the curve for 20° C., the only one that covers the complete range of composition from 0% to 100%, it is seen that a maximum in the density must occur at a composition above 70%.

In Fig. 2, the logarithm of the viscosity is plotted against the percentage of sulphur trioxide for the mixtures in Series *B*. The results at 0°, 10° and 20° C., the only temperatures at which mixtures containing more than 60% SO₃ could be investigated because of crystallization, indicate that a maximum in the viscosity-composition curve occurs at about 60% SO₃. Although this composition corresponds approximately to the formula HSO₃Cl · 2SO₃, the existence of a maximum in the viscosity-composition curve at this point is not necessarily indicative of compound formation. Many mixtures are known (1) that exhibit such a maximum, in the absence of the formation of definite compounds.

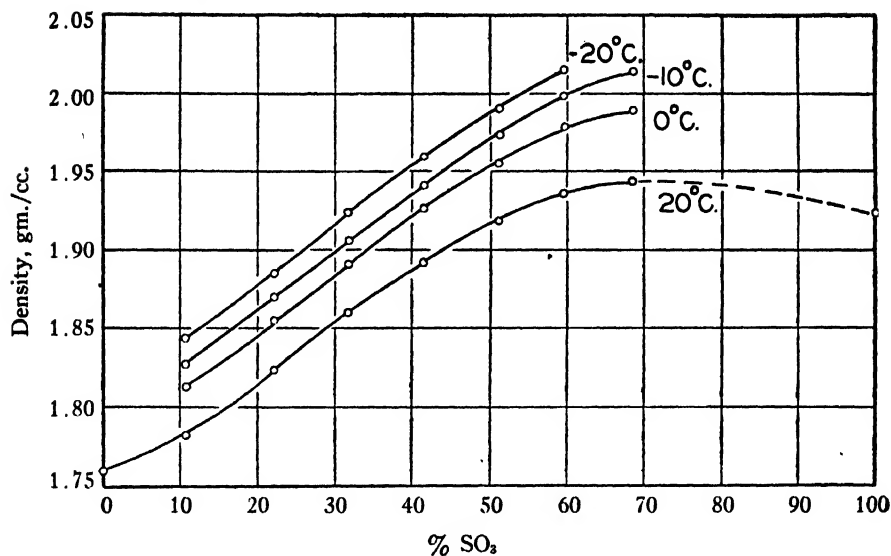


FIG. 1. Densities of chlorosulphonic acid - sulphur trioxide mixtures.

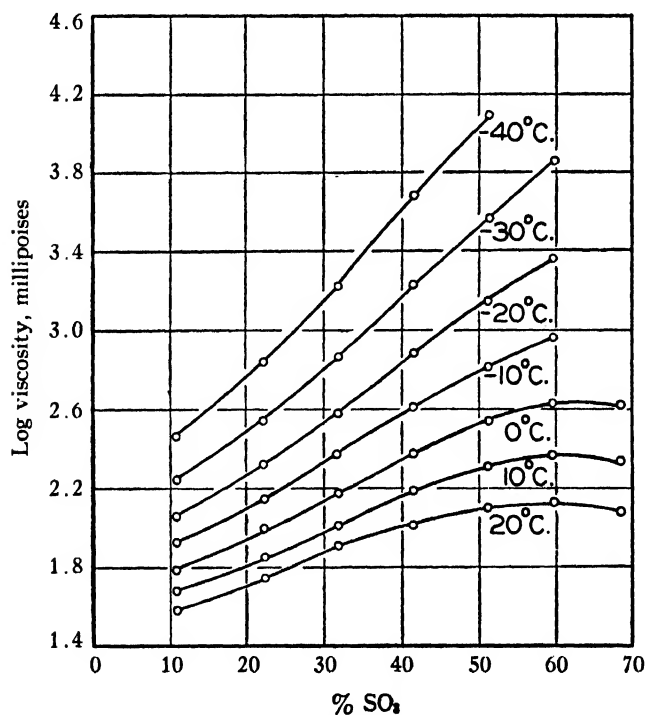


FIG. 2. The logarithm of the viscosity of chlorosulphonic acid - sulphur trioxide mixtures.

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A STUDY OF THE PRO-KNOCK ACTIVITY OF VARIOUS SUBSTANCES¹

By J. D. B. OGILVIE,² S. G. DAVIS³, A. L. THOMPSON,⁴ W. T. GRUMMITT,⁵
AND C. A. WINKLER⁶

Abstract

Compounds that cause an increase in the knocking tendency of gasolines are of two main types: (1) those such as dichloromethylarsine, cacodyl chloride, and arsenic tribromide, which counteract the effect of antiknock compounds present, and (2) those which, in addition, have some effect on the base stock, such as chloropicrin, bromopicrin, and bromine. Halogens, nitrites, nitro compounds and elements of Group V add to the pro-knock properties of a molecule. A long chain and an asymmetric molecule are effective structures. Pro-knock neutralized the effect of the antiknock but the concentration bore no direct relation to the antiknock concentration. Compounds of the first type showed greatest effect in fuels of high lead susceptibility brought up to a high octane rating with lead tetraethyl from a low octane base stock. They were similarly effective in counteracting iron carbonyl, but had no effect on aniline. Compounds of the second type effectively counteracted aniline, and when added to Diesel fuels showed a marked increase in the cetene number.

Introduction

The combustion of hydrocarbons is a complex process, as indicated by the variety of products that can be isolated. Most investigators are agreed that the mechanism is of the chain reaction type (1, p. 2927; 2; 3). The reaction chain may divide or branch, giving rise to new centers of activity. The process may then be expected to be highly susceptible to the influence of active catalysts and of changes in the temperature, pressure, and other conditions prevailing in the combustion chamber. An accumulation of extremely active chain carriers or other active intermediate products may occur during the early stages of the burning and give rise to a knocking type of combustion. This is a violent detonation of the last portion of the charge and occurs in internal combustion engines mainly when the engine is operating at high compression ratios and at low speed due to heavy load (4; 5, p. 3024; 7).

The variation in the knocking propensity of gasolines of various chemical compositions is well known (5, p. 3024; 6; 7), in particular the effects of such factors as the molecular chain length and branching, the degree of unsaturation,

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and the cyclic or aromatic nature of the fuel. The octane rating for comparison of the knocking characteristics of gasolines and its measurement requires no discussion here.

The action of antiknock compounds such as lead tetraethyl (8, p. 2911; 9, p. 692; 10), iron carbonyl (11, 12) and aniline (14) is also a matter of common knowledge. When present in small quantities these compounds result in a considerable improvement in the combustion characteristics of gasolines, from the point of view of power developed by, and smoothness of operation of, the engine. The action of pro-knock compounds is less well known, although substances such as ethers (12), peroxides (15), and organic nitrites, nitrates, and nitro compounds (13, 16, 17) are reported to promote knocking when present in a gasoline in low concentrations.

The investigations reported herein follow two lines of approach:

- (a) A study of the relative pro-knock activity of various compounds by determining the concentrations necessary to cause a 10 octane decrease in the rating of an 80 octane aviation fuel, particularly when the pro-knock was introduced into the air intake of an internal combustion engine.
- (b) A study of the effects of various pro-knock compounds on leaded and unleaded gasolines of different base stocks to observe their effects on these various types of fuels, and to obtain a clearer picture of the modes of action of the pro-knock substances.

The Pro-Knock Activity of Various Compounds

Preliminary Experiments

For the preliminary experiments a 1933 model Chevrolet engine was used. This was operated with a suitable braking arrangement at low speed and full throttle. Under these conditions the engine was extremely sensitive to pro-knock compounds. The addition agents were introduced into the air intake of the engine by placing a piece of gauze, wetted with the material, over the intake pipe. Some 197 compounds were tested. Those that caused knocking were investigated further. Measured quantities were introduced by displacement from a burette and subsequent atomization and evaporation in the air intake of the engine. The audibility of knock was used to compare the activity of various materials.

Procedure

Later work was done using an Ethyl Knock Testing Engine, Type 30B. This machine, although obsolete for routine laboratory testing, proved to be quite satisfactory. Results obtained in checking the octane ratings of gasoline agreed closely with those determined by the supplier. Operating conditions were those recommended in the operating manual for fuels in the octane range under study.

For every compound examined at least five octane determinations were necessary to establish a curve of octane decrease with concentration. Since the standard method of determining the octane ratings takes about two hours, it was desirable to decrease this time to speed up the investigation. Although the knockmeter reading for a gasoline of given octane rating may vary appreciably over the time necessary to complete the investigation of one addition agent, it was found that throughout this period the knockmeter range for two fuels of octane rating, say 10 units apart, remained essentially constant. Consequently the procedure adopted was as follows.

- (a) Calibration of knockmeter over the desired range using standard reference fuels. A plot of knockmeter change versus octane change was made.
- (b) Determination of the knockmeter reading for the basic fuel. (Each new shipment of gasoline was standardized by the usual Co-operative Fuel Research Method.)
- (c) Alternate determination of the knockmeter readings for the several tests on an adulterant and on the base fuel. The octane change was readily determined from the calibration.
- (d) The calibration was checked daily or when it appeared to have changed.

Since solid, liquid, and gaseous compounds were investigated as adulterants, various techniques were required to admit their vapors into the air consumed by the engine. The apparatus used is shown diagrammatically in Fig. 1.

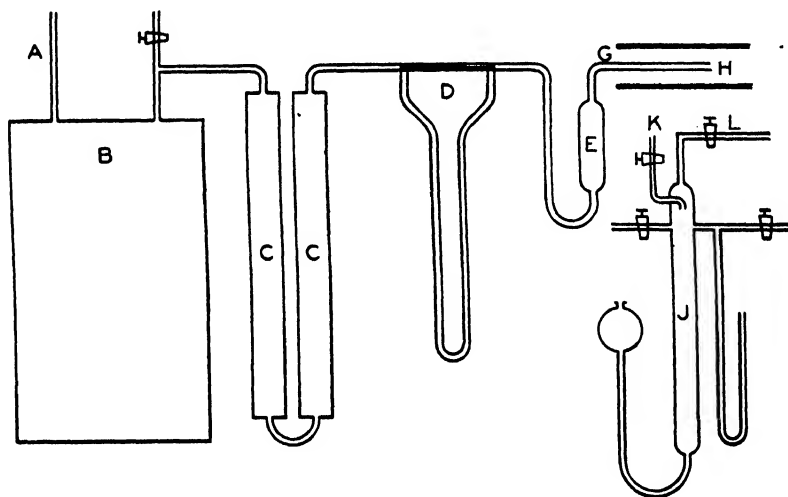


FIG. 1. Apparatus for introducing adulterants. A, compressed air supply; B, surge capacity; C, calcium chloride and phosphorus pentoxide drying tubes; D, capillary type flow-meter; E, pycnometer containing liquid adulterant; G, inlet tube to knock testing engine; H, air intake of engine; J, burette containing gaseous adulterant; K, to mercury or sulphuric acid displacing liquid reservoir; L, inlet tube to engine.

1. *Liquids*—were introduced by bubbling a small regulated stream of dry air through the compound contained in a pycnometer fitted with ground glass caps. When necessary the pycnometer was heated electrically or cooled by a dry ice and acetone bath. The engine was operated for 10 min. at each of five concentrations of adulterant, knockmeter readings being recorded. The concentration was regulated by the air stream and determined by the loss in weight of the pycnometer. The concentration necessary to cause a 10 octane drop was determined from a plot of octane decrease versus concentration.
2. *Solids*— were introduced similarly, using a horizontal pycnometer. Electrical heating was employed when necessary.
3. *Gases*— were added to the air stream by displacement from a burette attached to the inlet tube. Atmospheric pressure was maintained by a suitable leveling bulb and manometer system. In some cases the gas was diluted with air to a known concentration before displacement.

For solution work a stock solution of the adulterant in the basic fuel was made, and diluted portions were tested in progressively increasing concentrations until a 10 octane drop occurred. The concentration could be expressed in terms of the air consumption from the air-fuel consumption ratio curve obtained experimentally.

The gasoline used in this study was an 80.5 octane fuel leaded from a 72.5 octane aviation base stock using about 1.5 cc. of lead tetraethyl per U.S. gallon.

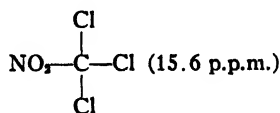
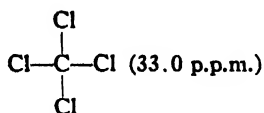
Adulterants were obtained from a variety of sources, a considerable number being prepared by the division of organic chemistry, McGill University, under the direction of Dr. R. V. V. Nicholls.

Results

The data obtained on the concentration of adulterant, expressed as parts per million of the air consumed by the engine, to cause a 10 octane decrease are recorded in Table I. The most effective materials of those studied are dichloromethylarsine (3.8 p.p.m.), arsenic tribromide (4.6 p.p.m.), cacodyl chloride (4.2 p.p.m.), lewisite (4.6 p.p.m.), and arsenic trichloride (5.8 p.p.m.). Other arsenic and phosphorus halides and oxyhalides are very effective and also some halogen-nitro substituted hydrocarbons. From the data obtained the following deductions may be made.

(1) The middle Group V elements of the periodic table possess the greatest pro-knock activity. The decreasing order of activity appears to be arsenic, phosphorus, nitrogen, and antimony. Vanadium in Group V(a) is between arsenic and phosphorus in pro-knock properties, as is its atomic weight. These elements are most effective as the halide or oxyhalide or in metallo-organic

molecules with halogens also present. Nitrogen in organic nitrites, nitrates, and nitro compounds shows considerable effectiveness. The inclusion of a nitro group in an organic halide greatly enhances the effect of the halogen, e.g.,



(2) The halogens possess powerful pro-knock tendencies by themselves and in combination with other elements. The order of decreasing effectiveness, both in the elemental and combined state, appears to be: bromine, chlorine, iodine, and fluorine. Both organic and inorganic halogen compounds are effective; for example, arsenic trichloride and chloropicrin. This would indicate, as do the data on arsenic, that the element itself rather than the type of linkage is important. Among the chloromethanes and chloroethanes, the activity increases with the number of chlorine atoms in the molecule. The tri-, penta-, and oxychlorides of phosphorus or arsenic have essentially similar pro-knock activity. Iodine mono- and trichlorides are considerably more effective than either iodine or chlorine as elements.

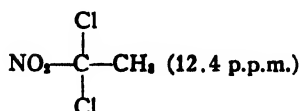
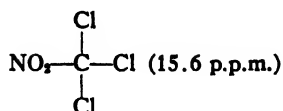
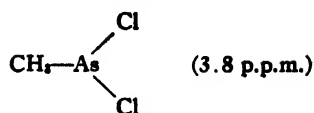
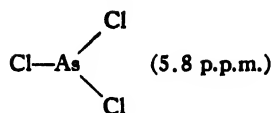
(3) Among the Group VI elements, chromium, as the oxychloride, is as effective as phosphorus. Sulphur is also quite effective, as shown by the compounds sulphur chloride (10.6 p.p.m.), thionyl chloride (15.1 p.p.m.), methyl disulphide (37 p.p.m.) and *n*-butyl mercaptan (108 p.p.m.). The sulphide linkage appears to be more effective than the mercaptan. Ethyl sulphite is more effective than ethyl nitrate. The thionitrites are not as effective as the nitrite, and the thiocyanate is much more effective than the isothiocyanate. Selenium seems even more effective than sulphur when used as the oxychloride (8.3 to 15.1 p.p.m.).

(4) Other elements that appear to show good pro-knock activity are aluminum (aluminum chloride, 14.5 p.p.m.) and silicon (silicon tetrachloride, 33.0 p.p.m.).

(5) The metal naphthenates, when added in solution, give a good comparison of the relative activities of the metals themselves since the naphthenate radical has very slight antiknock properties. Mercury and vanadium are particularly effective and chromium, nickel, iron, and copper less so. Magnesium, zinc, lead, manganese, and cobalt are not very effective.

(6) Studies of the organic halides, nitrites, and nitro compounds show that increasing the straight chain length in aliphatic compounds increases the pro-knock activity of the molecule (e.g., chlorides—methyl 195, ethyl 156, heptyl 88; nitrites—methyl 300, ethyl 200, heptyl 49). Branching, as illustrated by the butyl and amyl nitrites, decreases the effectiveness of the compound.

(7) The inclusion of a methyl group in arsenic trichloride, as dichloromethylarsine, results in increased activity. This is true, also, with chloropicrin and 1,1-dichloronitroethane.



(8) Aromatic compounds are, in general, poor pro-knock materials. Benzene sulphonyl chloride requires 54 p.p.m. to cause a 10 octane decrease even with the active sulphonyl chloride substituent.

TABLE I
PRO-KNOCK CONCENTRATIONS FOR 10 OCTANE DECREASE
(Expressed in parts per million of air consumed)

Compound	In air, p.p.m.	In fuel, p.p.m.	Compound	In air, p.p.m.	In fuel, p.p.m.
<i>Organic nitrites</i>					
Methyl nitrite	300.0		Nitrite of <i>sec</i> -butyl carbinol	92.0	
Ethyl nitrite	200.0		Nitrite of diethyl carbinol	93.0	
<i>n</i> -Butyl nitrite	82.5	67.0	<i>n</i> -Propyl nitrite	125.0	
Isobutyl nitrite	107.0		<i>n</i> -Heptyl nitrite	49.0	
<i>sec</i> -Butyl nitrite	88.0		<i>n</i> -Octyl nitrite	45.0	62.5
<i>tert</i> -Butyl nitrite	96.5		Trichloroethyl nitrite	76.0	
<i>n</i> -Amyl nitrite	62.0		<i>n</i> -Butyl thionitrite	130.0	
Isoamyl nitrite	63.0	74.5			
<i>tert</i> -Amyl nitrite	92.0				
<i>Organic halides</i>					
Monochloromethane	195.0		Trichloroethylene	51.0	
Dichloromethane	68.0	68.5	Tetrachloroethylene		41.5
Trichloromethane (chloroform)	44.0	62.5	<i>tert</i> -Butyl chloride		45.5
Carbon tetrachloride	33.0	40.0	<i>n</i> -Heptyl chloride	88.0	
Difluorodichloromethane (freon)	125.0		Benzyl chloride	141.0	
Dibromomethane	48.3		Oxalyl chloride	45.1	
Monochloroethane	156.0	156.0	Carbonyl chloride (phosgene)	120.0	
1,1-Dichloroethane	78.0		Ethyl hypochloride	135.0	
1,1,2-Trichloroethane	55.0	67.0	Cyanogen bromide	113.0	
1,1,2,2-Tetrachloroethane		40.5	Chloral cyanohydrin	37.0	
Pentachloroethane		27.0	Trichloroacetyl chloride	28.0	
Hexachloroethane	16.4		Ethylene chloronitrite	150.0	
1,2-Dichloroethylene		63.0	Trichloroethyl nitrite	76.0	
			Diethylchloramine	164.0	

TABLE I—*Concluded*
 PRO-KNOCK CONCENTRATIONS FOR 10 OCTANE DECREASE—*Concluded*
 (Expressed in parts per million of air consumed)—*Concluded*

Compound	In air, p.p.m.	In fuel, p.p.m.	Compound	In air, p.p.m.	In fuel, p.p.m.
<i>Halogens and inorganic halides</i>					
Chlorine	40.0		Selenium oxychloride	8.3	43.5
Bromine	16.2		Phosphorus trifluoride	31.5	
Iodine	56.0		Phosphorus pentafluoride		41.1
Hydrogen fluoride	90.0		Phosphorus trichloride	8.6	
Hydrogen chloride	30.0		Phosphorus pentachloride		6.5
Hydrogen bromide	62.0		Phosphorus oxychloride	8.7	26.5
Iodine monochloride	18.5		Arsenic trifluoride	11.0	
Iodine trichloride	11.8		Arsenic trichloride	6.8	
Iodine monobromide	15.5		Arsenic pentachloride	6.1	
Boron trifluoride	115.0		Arsenic tribromide	5.6	
Aluminium trichloride	14.5		Vanadium chloride-		
Silicon tetrachloride	23.0	16.0	oxychloride (1 : 1)	7.1	
Sulphur hexafluoride	195.0		Chromium oxychloride	7.7	
Sulphur chloride	10.6		Antimony pentachloride	6.1	
Thionyl chloride	15.1				
<i>Nitro-halogen substituted hydrocarbons</i>					
Tetranitromethane	88.0	38.5	Trichloronitromethane		
Bromonitromethane	21.5		(chloropicrin)	15.5	12.0
Monobromotrinitro-			1,1-Dichloro-1-nitro-		
methane	15.7	17.0	ethane	12.5	12.0
Dibromodinitromethane	11.4		1-Chloro-1-nitroethane	28.8	36.0
Tribromonitromethane			2-Chloro-2-nitropropane	91.4	41.0
(bromopicrin)	8.2	13.0			
<i>Sulphur compounds</i>					
Methyl disulphide	37.0		Methyl thiocyanate	115.0	
Ethyl sulphide	100.0		Methyl isothiocyanate	285.0	
n-Butyl mercaptan	108.0		n-Butyl thionitrite	130.0	
Carbon disulphide	205.0		Thionyl chloride	15.1	
Ethyl sulphide	100.0	143.0	Sulphur hexafluoride	195.0	
Benzene sulphonyl chloride	54.0		Sulphur chloride	10.5	
n-Propyl sulphone	132.0				
<i>Miscellaneous</i>					
Dichloromethylarsine	3.8	5.0	Ethyl orthosilicate	23.6	
Caodyl chloride	4.2	5.0	Acetyl nitrate	140.0	
Lewisite		4.6	2-Nitrobutanol acetate	310.0	
<i>Metal naphthenates</i>					
	Octane decrease at 0.3 gm./ 100 cc. fuel			Octane decrease at 0.3 gm./ 100 cc. fuel	
Potassium naphthenate	(Insoluble)		Vanadium naphthenate	10.0	
Copper naphthenate	2.3		Chromium naphthenate	4.2	
Magnesium naphthenate	1.2		Manganese naphthenate	1.8	
Zinc naphthenate	0.8		Iron naphthenate	3.0	
Mercury naphthenate	16.0		Cobalt naphthenate	1.5	
Lead naphthenate	0.8		Nickel naphthenate	3.3	

Effect of Larger Concentrations of Pro-knock

Procedure

The procedure followed was similar to that previously employed except that where octane decreases of more than 10 units were obtained, a stepwise reduction in compression pressure was necessary for the various octane ranges. This is a valid procedure, since overlapping the ranges and plotting the results shows a smooth curve. Reference fuels were used to bracket each reading on the knockmeter in the lower ranges.

For this work an 80.5 octane aviation fuel was used, leaded to this value from a base stock of 64 octane units.

Results

The octane decreases resulting from various concentrations of pro-knocks are shown in Table II. Some of the results are illustrated further in the

TABLE II

OCTANE DECREASE OF LEADED AND UNLEADED NAPHTHA BY VARIOUS PRO-KNOCK AGENTS

(Octane rating of base stock 16.5 units less than that of leaded fuel)

Chloropicrin				Bromine				Arsenic trichloride		Phosphorus trichloride	
Leaded		Unleaded		Leaded		Unleaded		Leaded (unleaded—no effect)		Leaded (unleaded—no effect)	
Conc., p.p.m.	Octane decr.	Conc., p.p.m.	Octane decr.	Conc., p.p.m.	Octane decr.	Conc., p.p.m.	Octane decr.	Conc., p.p.m.	Octane decr.	Conc., p.p.m.	Octane decr.
6.0	6.0	30.0	5.0	14.0	16.0	20.0	1.0	3.5	10.0	4.5	11.0
15.5	15.0	42.0	6.5	20.0	17.5	41.5	3.0	6.0	14.0	12.0	14.0
25.0	19.5	58.0	7.5	25.0	19.0	70.0	3.5	12.0	16.5	16.7	15.7
82.0	29.5	79.0	10.0	45.0	19.5	85.0	4.5	24.0	17.0	35.0	17.0
90.0	31.0	97.0	12.0	80.0	21.0			64.0	17.0	65.0	17.7
Antimony pentachloride		Diphenylchloroarsine		Sulphuryl chloride		Bromopicrin		Phosphorus oxychloride		Methyl bis- β -chloroethylamine	
Leaded (unleaded—no effect)		Leaded		Leaded		Leaded		Leaded		Leaded	
Conc., p.p.m.	Octane decr.	Conc., p.p.m.	Octane decr.	Conc., p.p.m.	Octane decr.	Conc., p.p.m.	Octane decr.	Conc., p.p.m.	Octane decr.	Conc., p.p.m.	Octane decr.
5.8	5.3	6.3	10.0	10.0	5.0	7.0	8.5	12.8	9.5	15.0	8.0
7.3	8.4	11.0	14.5	34.0	13.0	11.0	10.5	20.0	14.0	25.0	13.0
11.2	13.6	16.7	15.5	45.0	15.0	13.0	13.5	22.0	14.0	32.0	15.0
15.3	14.0	19.0	16.0	90.0	17.0	14.0	16.0	30.0	14.5	50.0	16.5
23.0	15.0	40.0	16.0			21.0	19.0			85.0	16.5

graphs in Fig. 2. The pro-knock activity of arsenic trichloride and phosphorus trichloride ceases to increase with concentrations greater than 14 p.p.m. This rather abrupt change of slope in the curve occurs at an octane

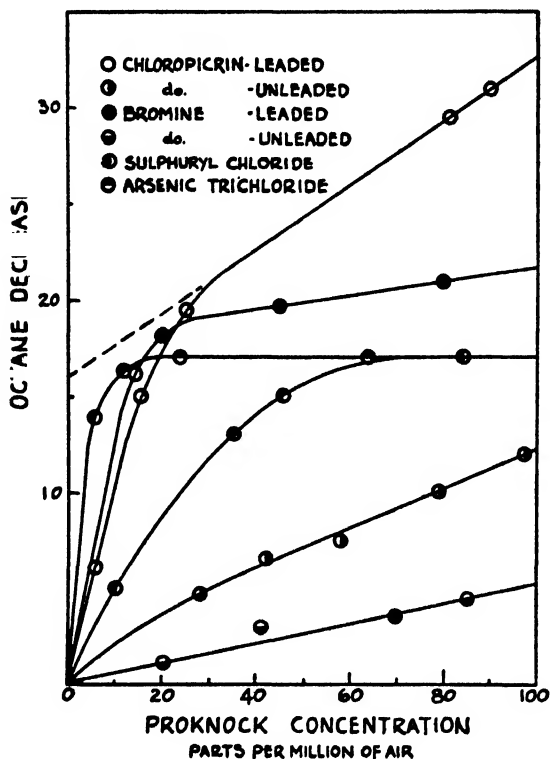


FIG. 2. Effect of pro-knock concentration on octane number of gasolines containing no lead tetraethyl (octane number = 64) and containing lead tetraethyl (octane number = 80.5).

decrease of about 16.5 units. Only large concentrations of phosphorus trichloride (of the order of 1000 p.p.m.) give any increase in knock with an unleaded fuel. Large concentrations of arsenic trichloride have no effect with an unleaded gasoline. Similar behavior is exhibited by diphenylchloroarsine, phosphorus oxychloride and methyl bis- β -chloroethylamine in decreasing order of effectiveness. Antimony pentachloride and thionyl chloride are somewhat similar except that the first attains a maximum about 1.5 units short of the others and falls off, while the second is very gradual. On the other hand, bromine, chloropicrin, and bromopicrin possess a different pro-knock characteristic. The change is more gradual and they have some influence on unleaded fuel. The straight line relation at high concentrations of chloropicrin for the leaded fuel parallels the relation between concentration and octane decrease for the unleaded fuel and extrapolates to a 16.5 octane decrease at zero concentration.

From these considerations it is evident that the effect of certain of the pro-knock compounds is primarily to overcome the effect of lead tetraethyl on the fuel. Thus it becomes apparent that the octane decrease produced by the pro-knock depends, to a large extent at least, on the difference between the octane rating of the base fuel and that of the leaded gasoline.

Aside from this conclusion there are other interesting points. With antimony pentachloride the equilibrium



could be rapidly shifted to the right under operating conditions. It is probable that antimony in both the penta- and trivalent forms is capable of overcoming the effect of the lead tetraethyl, but trivalent antimony is the more stable form and possesses good antiknock properties (18) which are observed at the higher concentrations of the adulterant.

Diphenylchloroarsine possesses about the same activity as arsenic trichloride which demonstrates the specific action of the arsenic atom in compensating the influence of added lead tetraethyl.

The relation between the octane decrease produced by the pro-knock and the difference in octane ratings of the base and leaded fuels was studied in more detail by determining the effect of arsenic trichloride and chloropicrin on a graduated series of leaded gasolines.

Shell naphtha, an aviation base of 64 octane, was used. Portions were leaded with 0.25, 1.0, 2.0, and 4.0 cc. of lead tetraethyl per U.S. gallon. Octane ratings were determined on the engine to its maximum range and thereafter from a lead susceptibility chart (20, p. 2937) kindly supplied by the Shell Oil Company. Various concentrations of pro-knock were added and the octane drop determined.

The results are plotted in Fig. 3. With arsenic trichloride a family of curves is obtained, each curve sloping off at the octane rating of the base fuel. Further increases in concentration of the pro-knock have no effect. The concentration of arsenic trichloride at the point of intersection represents complete counteraction of the effect of the lead added. Comparison with the concentrations of lead tetraethyl, and with the antiknock effect produced by the lead tetraethyl, gives the following ratios:

Arsenic trichloride concentration	1 : 2.1 : 3.2 : 4.0
Lead tetraethyl concentration	1 : 4 : 8 : 16
Antiknock effect of lead tetraethyl	1 : 2.5 : 3.4 : 4.0

This would indicate that such pro-knocks counteract the antiknock effect of the lead tetraethyl rather than the tetraethyl itself.

For arsenic trichloride and for lower concentrations of phosphorus trichloride a straight line relation exists between the maximum octane change and the volume per cent pro-knock just sufficient to produce this change. Also

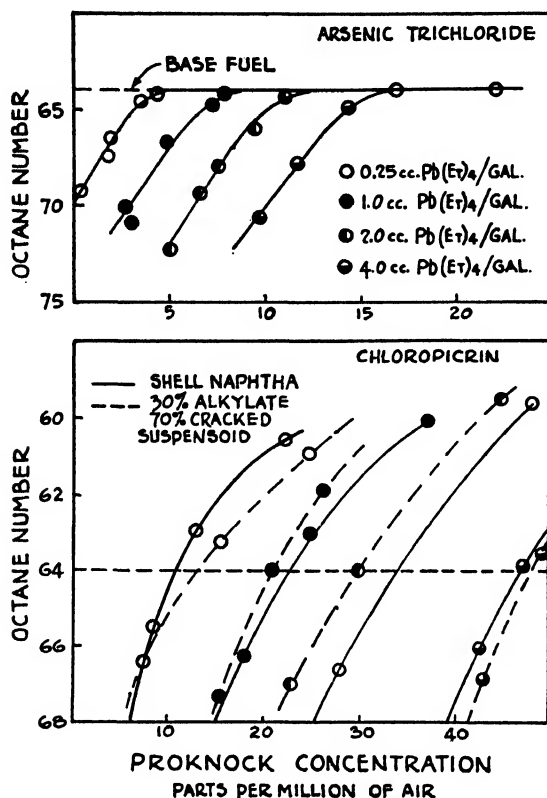


FIG. 3. Relation of pro-knock concentration to octane number decrease for leaded and base stocks (legends common to both graphs).

illustrated (Fig. 4) is the relation between the concentration of lead tetraethyl and the concentration of pro-knock to neutralize the octane improvement resulting from the lead tetraethyl. The molar relations are shown in Fig. 5 and in addition a curve to show the relative atomic effects of lead and arsenic. It is obvious that the action of pro-knock compounds such as arsenic trichloride and phosphorus trichloride is a neutralization of the antiknock effect of the lead tetraethyl and not a neutralization of the lead tetraethyl itself.

The action of chloropicrin, which has some pro-knock effect on the base fuel, was also studied in greater detail. The family of curves obtained (Fig. 3) when the octane decrease is plotted against the concentration of chloropicrin does not show the falling-off at the octane rating of the base stock, but rather the pro-knock effect continues without a break in the curve. The intersections were treated similarly to those of the arsenic trichloride curves, in Figs. 4 and 5.

The molar relation between pro-knock and antiknock concentration for chloropicrin is a straight line, unlike that of arsenic trichloride, which falls off rapidly at higher lead contents.

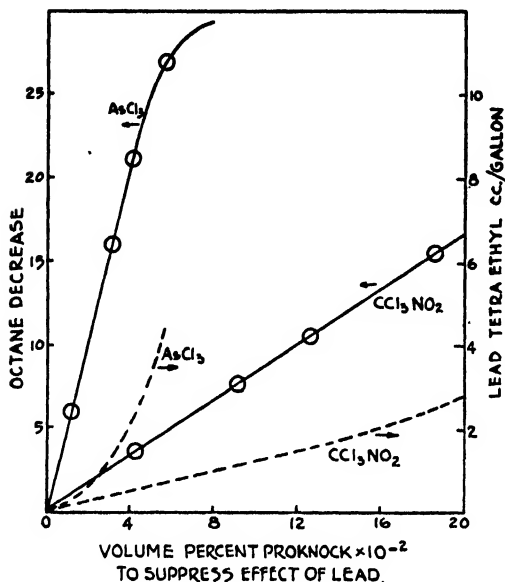


FIG. 4.

FIG. 4. Relation between concentration of pro-knock to suppress the effect of lead tetraethyl, and (a) the decrease in octane number corresponding to the suppression, (b) the lead tetraethyl content of the gasoline.

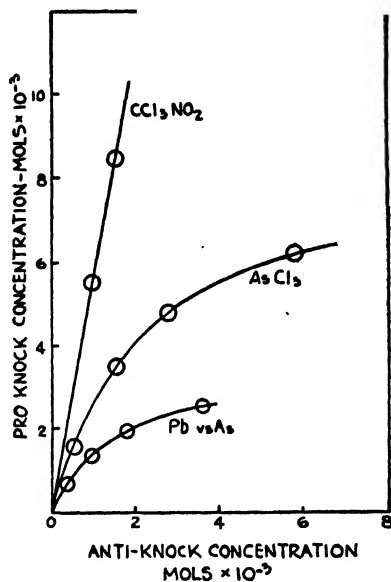


FIG. 5.

FIG. 5. Molar relations between antiknock concentration and concentration of pro-knock to suppress the effect of the antiknock.

These results were obtained using Shell naphtha base fuel. Similar curves were obtained for a gasoline of 70% cracked suspensoid and 30% alkylate.

Effect of Composition of Base Stock

Since automotive fuels are made up from gasolines of various chemical compositions, a study was made of the effects of pro-knock concentration and lead content for fuels of various typical base stocks. It is well established that the octane increase obtained using lead tetraethyl varies considerably with the base stock. A measure of this difference in the response of gasolines to lead tetraethyl is the lead susceptibility of the gasoline, i.e., the increase in octane rating per cubic centimeter of lead tetraethyl added (19). This lead response for different fuels increases in the following order: cracked, straight run, and natural gasolines and isopentane. The lead susceptibility for any gasoline decreases as its octane number is raised, but possibly this is due to the knock testing standards. An increase from 80 to 85 octane units indicates relatively greater improvement in engine performance than from 50 to 60 units.

From this it might be expected that the greatest octane decrease possible would be in a gasoline of high lead susceptibility, leaded from a low octane base stock. Similar experiments to those described in the previous section but using gasolines of base stocks of various compositions show the maximum octane drops possible through use of pro-knock compounds and the concentrations required.

Procedure

A series of fuels was made up by adding increasing proportions of benzene to Shell naphtha, a base stock of 64 octane units. Each of these was treated with various amounts of lead tetraethyl. Arsenic trichloride was used as the adulterant in these experiments.

Results

In Fig. 6 are graphs showing the octane number decrease corresponding to complete neutralization of the lead tetraethyl as a function of the pro-knock concentration necessary to cause this decrease.

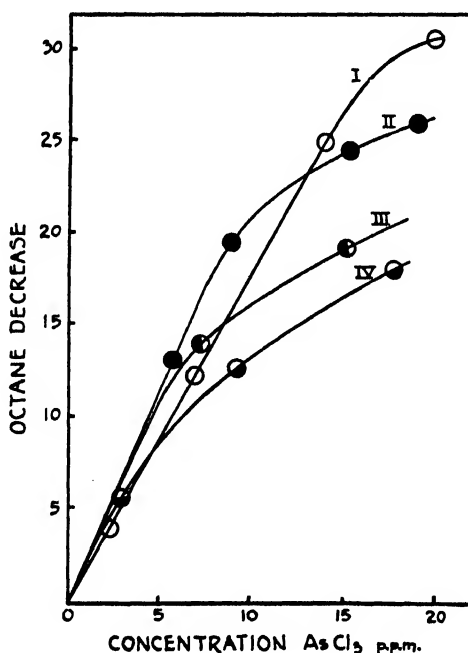


FIG. 6. Effect on pro-knock activity of decreasing the lead susceptibility and increasing the octane number of the base fuel with benzene.

N = Octane number
 S = Lead susceptibility

- I N = 64 S = 3.0 (Shell naphtha)
 II N = 67 S = 2.5 (Shell naphtha + 15% benzene)
 III N = 69 S = 2.3 (Shell naphtha + 25% benzene)
 IV N = 75 S = 1.8 (Shell naphtha + 40% benzene)

As the concentration of benzene is increased, the octane rating of the base stock increases as its lead susceptibility is decreased. This appears to make it easier for the pro-knock to effect a given octane decrease in the initial stages. Similar results were obtained using alkylate in place of benzene in the base stock. The results illustrate that the important characteristics of a fuel in relation to the ease with which a pro-knock could effect a decrease in octane rating is not so much the composition of the fuel but the inherent values of lead susceptibility and base octane number.

The relative importance of base octane number and lead susceptibility was investigated further. In Fig. 7 the effect of the lead susceptibility of a

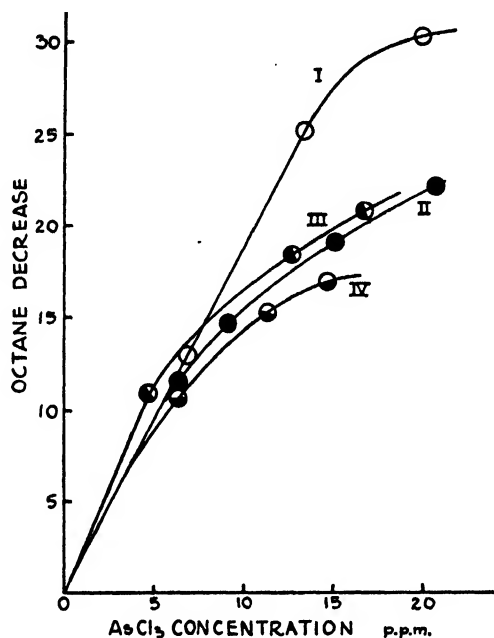


FIG. 7. Relation of pro-knock concentration to octane number decrease for gasolines of different lead susceptibilities but the same octane rating.

N = Octane number
S = Lead susceptibility

- I *N* = 64 *S* = 3.0 (Shell naphtha)
 II *N* = 64 *S* = 2.3 (40% benzene + 60% straight run)
 III *N* = 69 *S* = 2.3 (25% benzene + 75% Shell naphtha)
 IV *N* = 69 *S* = 1.2 (40% benzene + 60% suspensoid)

fuel at constant octane rating is illustrated. At high lead susceptibility a large drop in octane rating is caused by a relatively small arsenic trichloride concentration completely nullifying the effects of the lead tetraethyl. This effect decreases as the lead susceptibility decreases. In a 64 octane base stock the reduction in octane change as between fuels of lead susceptibility of 3.0 and

2.3 (Curves I and II) is much greater than the corresponding reduction as between fuels of lead susceptibility of 2.3 and 1.2 in a 69 octane base stock (Curves III and IV).

The effect of the octane rating of the base stock is illustrated in Fig. 8, in fuels of similar lead susceptibility. Curves III and IV show the effect of wide variation in octane rating of the base stock. Curve III shows that for blends

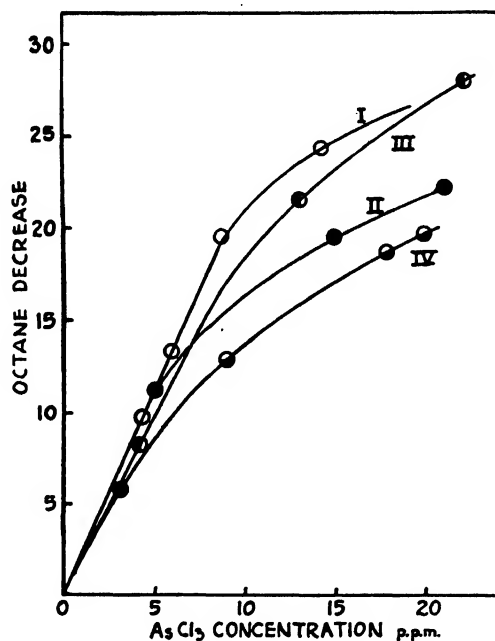


FIG. 8. Relation of pro-knock concentration to octane number decrease for gasolines of different octane ratings but the same lead susceptibility.

N = Octane number

S = Lead susceptibility

I $N = 67$ $S = 2.5$ (Shell naphtha + 15% benzene)

II $N = 80$ $S = 2.6$ (Shell Reference Fuel)

III $N = 49$ $S = 1.8$ (Heavy straight run)

IV $N = 75$ $S = 1.8$ (Shell naphtha + 40% benzene)

of low base octane number whatever increase is effected by the lead tetraethyl is readily nullified by pro-knock. Thus it would appear that in general the activity of a pro-knock specific for counteracting lead is decreased with increase in the base octane number of the fuel.

Counteraction of Various Antiknock Compounds

Tests made to observe the activity of pro-knocks in fuels whose octane ratings had been increased by antiknock agents other than lead tetraethyl show similar results, as illustrated by the curves in Fig. 9.

Chloropicrin is effective in counteracting nickel carbonyl (I) in concentrations similar to those required to counteract lead tetraethyl, but bromine requires considerably larger concentrations (III). The octane drop effected

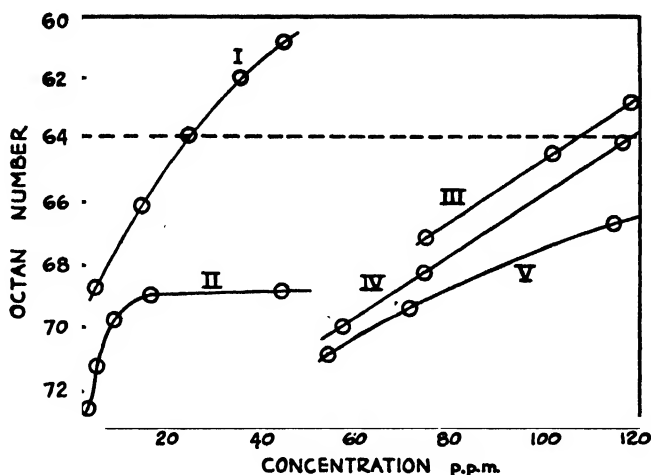


FIG. 9. Relation between pro-knock concentration and octane number decrease with gasolines containing antiknock agents other than lead tetraethyl.

- I Chloropicrin (pro-knock) - nickel carbonyl (antiknock)
- II Arsenic trichloride (pro-knock) - nickel carbonyl (antiknock)
- III Bromine (pro-knock) - nickel carbonyl (antiknock)
- IV Chloropicrin (pro-knock) - aniline (antiknock)
- V Bromine (pro-knock) - aniline (antiknock)

by arsenic trichloride falls off rapidly with increasing concentrations of the pro-knock and reaches a maximum within five octane units of the base stock. Apparently the action of this antiknock cannot be completely counteracted by arsenic trichloride.

Chloropicrin and bromine also effectively counteract the antiknock effect of aniline (IV and V), whereas arsenic trichloride has no effect. Presumably this is due to a difference in antiknock action and indicates that organometallic pro-knocks cannot affect organic antiknocks.

The molar relations between the equivalent concentrations of pro- and antiknock compounds are shown in Fig. 10, for counteraction of both lead tetraethyl and iron carbonyl by arsenic trichloride. Arsenic trichloride is just as efficient in counteracting iron carbonyl as lead tetraethyl. Here again the arsenic trichloride concentration is related to the octane change brought about by the carbonyl and not necessarily to the amount present. The action of lead tetraethyl and iron carbonyl would thus appear to be the same, although it requires five times as much iron carbonyl in this particular fuel. The fact that the counteraction of lead tetraethyl and iron carbonyl by arsenic tri-

chloride may be illustrated by a single curve indicates that the mechanism of increasing and decreasing the octane rating is identical.

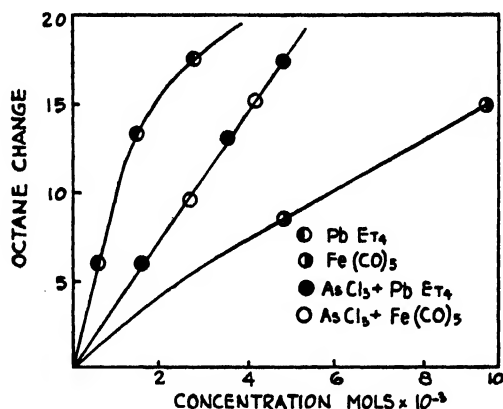


FIG. 10. Molar relations of anti- and pro-knock agents in Shell naphtha.

Miscellaneous Effects

Tests on the pro-knock activity of arsenic trichloride on dried and undried fuels indicate a slight impairment by the moisture present. With lewisite the hydrolysis had little effect.

The effect of engine temperature on the action of various pro-knock substances is not appreciable. The action of arsenic trichloride is reduced slightly at the higher concentrations of lead tetraethyl. Chloropicrin shows greater susceptibility to temperature change than bromine or arsenic trichloride. It is slightly more effective at lower jacket temperatures. This might be true in general for organic pro-knocks since they would be more rapidly decomposed at higher temperature.

The effect of octane decrease on the power developed was studied, using a recording wattmeter. An octane decrease of 10 units causes about a 5% decrease in the power developed by the engine. The power loss caused by the octane decrease due to pro-knock action is the same as that caused by the use of a correspondingly poorer fuel.

Several pro-knock substances such as amyl thionitrate and chloropicrin are known to improve the combustion characteristics of Diesel fuels. The results of some experiments on the effect of chloropicrin and diphenylchloroarsine are shown in Table III.

It may be seen that pro-knock compounds specific for counteracting lead tetraethyl are useless for the improvement of Diesel fuels. It is possible that bromopicrin, which is a better pro-knock compound than chloropicrin, would show correspondingly greater improvement in the Diesel fuel.

TABLE III

Fuel	Cetene number
Base Diesel fuel	44
Base plus chloropicrin, 1.62 gm./liter	48
“ “ “ 5.2 “	52
“ “ diphenylchloroarsine, 1.25 gm./liter	44
“ “ “ 3.75 “	43

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THE OXIDATION, IGNITION AND DETONATION OF FUEL VAPORS AND GASES

V. THE HYDROGEN ENGINE AND THE NUCLEAR THEORY OF IGNITION¹

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Abstract

It should not be possible, according to the nuclear theory of ignition, stated in Part IV, to obtain ignition in the body of a gaseous combustible mixture by any method of heating if it remain truly homogeneous while the temperature is raised. Such mixtures cease to be homogeneous when heated by sudden compression to the temperatures required for ignition because of the formation of finely divided carbon by pyrolysis of lubricating oil or of hydrocarbon vapor. The finely divided carbon provides nuclear centers of ignition in the gaseous mixture. Ignition due to finely divided carbon produced by pyrolysis of the lubricant is demonstrated by experiments with hydrogen as the fuel for a C.F.R. engine. The usual pre-ignition and severe knocking were obtained when the engine in normal condition was run on hydrogen, and it was impossible, as previously found by others, to use any but weak mixtures even at low compression ratios. When however the combustion space was decarbonized and thereafter maintained reasonably clear of fluffy carbon, hydrogen could be used as the sole fuel at any compression ratio up to the limit of 10 : 1 possible with the engine, and at any mixture strength ranging from very weak to very rich, while power output varied accordingly. Conversely pre-ignition and combustion knock reappeared when carbon dust was admitted with the combustible mixture.

Introduction

Hydrogen-air mixtures when used in an Otto cycle engine are heated by sudden compression and by contact with hot surfaces such as exhaust valves. The tendency of the mixture to 'detonate' or to explode prematurely in the usual conditions of operation limits the power and efficiency to relatively low values. Ricardo (12), using the E35 engine, cylinder diameter 4.5 in., found that if the mixture with air contained 50% only of the hydrogen required for combining proportions, a compression ratio of 7 : 1 could be used and the high thermal efficiency of 37.5% obtained. It was necessary to lower the compression ratio progressively as the hydrogen concentration was increased but even so it was not possible to use the mixture strength for maximum power. "If an attempt were made to run with a rich hydrogen-air mixture, violent pre-ignition occurred, accompanied by firing back in the carburetor, which rendered further running impossible. Even with the compression ratio lowered to 3.8 : 1 the same thing occurred". There seemed to be a limiting indicated mean effective pressure (I.M.E.P.) of 74 lb. per sq. in. Attempts to obtain higher values by increasing hydrogen concentration or by raising

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the compression ratio were always defeated by the onset of detonation or pre-ignition. The range of mixture strength usable with various engine fuels was discussed by Ricardo in a later publication (13, pp. 42–43) and, in respect of hydrogen, it was stated that "the range of burning could not be explored because, so soon as any excess of hydrogen was admitted, back firing occurred through the inlet valves". Ricardo's conclusions were confirmed by A. F. Burstall (1) even in respect of the I.M.E.P. having a limiting value of approximately 74 lb. per sq. in. The experiments of Egerton, Smith and Ubbelohde (4) with hydrogen as fuel for a Delco knock testing engine, cylinder diameter 2.5 in. only, demonstrated that knocking combustion was not restricted to engines having relatively large cylinders. Egerton (4, p. 517) attributed the detonation to nitrogen peroxide formed from the nitrogen of the air.

The combustion phenomena described by Ricardo and others are usually attributed to ignition of the hydrogen–air mixture by hot surfaces or to ignition being the final result of a chain reaction proceeding at the temperature attained by sudden compression. An alternative explanation is afforded by the nuclear theory of self ignition advanced in Part IV (10), the finely divided carbon for nuclear centers of ignition, as required by the theory, being provided by pyrolysis of the lubricating oil. Experiments made accordingly in the Heat Engine Laboratory of the University of Toronto and described in Section I show that hydrogen can be used as the fuel for an Otto cycle engine, in any mixture proportion with air and at compression ratios rising to 10 : 1, without pre-ignition or detonation if the concentration of finely divided carbon in the gaseous mixture be maintained at a relatively low value.

Section I

Experimental

The Co-operative Fuel Research Committee (C.F.R.) knock testing engine was used for the experiments with hydrogen. The bore is 3.25 in. and the stroke 4.5 in. The compression ratio can be varied from 4 to 10 : 1. The cylinder is maintained normally at a nearly constant temperature of 212° F. by the evaporation of distilled water at atmospheric pressure. The engine is connected to a d-c. main generator and to a similar auxiliary generator. Speed is controlled manually by adjusting the field excitation of the main generator and the electrical output absorbed by a resistor bank.

Lubrication.—The piston is fitted with three pressure rings and one oil scraper ring. A partial vacuum is created in the crank case by fitting the breather with a nonreturn flap valve that closes during the compression and exhaust strokes. The rate of oil consumption in the circumstances is so low that, after 100 hr. running, careful measurement is required to determine the quantity used. The oil in the crank case was maintained at a temperature of between 120° and 130° F. by a manually controlled electric heater. A commercial brand of S.A.E. 30, without 'additives', was used during the experiments.

Hydrogen Supply.—The standard horizontal carburetor with 9/16 in. diameter venturi and no throttle plate was used for the experiments. Hydrogen was admitted to the throat of the venturi through a 0.125 in. diameter hole in a screw which replaced the standard hold down screw of the unused cap jet. Hydrogen procured by electrolysis was supplied in the usual pressure bottles by the Dominion Oxygen Company, and contained not more than 0.3% of oxygen. The hydrogen passed through an adjustable pressure reducing valve, then through a fine adjustment needle valve to a circular square edged metering orifice in a thin plate and thence to the carburetor venturi. The rate of supply to the engine was taken to be proportional to the square root of the pressure difference, in inches of water, across the orifice.

Air Supply.—Air was taken in by the engine at laboratory temperature and the humidity not controlled. The standard air inlet to the carburetor comprises a short piece of $1\frac{1}{4}$ in. I.D. tubing ending in a 90° elbow into which is fitted a long inlet pipe ($20\frac{1}{4}$ in.) also $1\frac{1}{4}$ in. diam. Eight inches of the outer end is arranged as a silencer but the diameter of the tube is not reduced. The standard pipe inlet was on occasion replaced by a swirl chamber 6 in. diam. and $6\frac{1}{2}$ in. long provided with tangential inlets and outlets. The cover of one end was a 'push on' fit and blew off when back firing through the carburetor (induction ignition) occurred.

The Inlet Valve.—The standard inlet valve is fitted with a 180° shroud so arranged that the combustible mixture is given a swirling motion on entering the cylinder. The arrangement has been found of beneficial effect in respect of determinations of the relative antiknock values of gasolines, but it reduces volumetric efficiency and is not used in practice.

Definition of the Terms Used to Describe Abnormal Ignition or Combustion

Detonation knock describes an effect due to the self-ignition and explosion of the gas ahead of the flame (end gas). Eliminating the knock by retarding ignition gives rise to a *decrease* of power.

Combustion knock describes an effect due to an abnormally high rate of flame propagation. The knocking sound in the C.F.R. engine is similar to that heard when detonation occurs. Eliminating or reducing the knock by retarding ignition gives rise to an *increase* of power. This characteristic makes it possible to distinguish between combustion knock and detonation knock.

Induction ignition describes the effect obtained when the combustible mixture ignites before the inlet valve closes. The effect gives rise to explosions in the induction system and carburetor, the violence depending on mixture proportion and the volume involved. The explosions occur irregularly.

Pre-ignition is initiation of combustion after the inlet valve closes and before ignition by spark. If the ignition occurs sufficiently late in the compression stroke, the engine will run without spark ignition but generally at reduced power and for relatively short periods of time.

Preliminary Engine Experiments with Unclean Combustion Chamber

The experiments were begun with the engine as found. It had been run for some weeks on hydrocarbon fuels, generally leaded. The compression ratio was set at 5 : 1, the ignition timing at 30° advance, and the engine run at 900 r.p.m. for a warming up period of one hour on leaded gasoline. The gasoline was then shut off* and hydrogen admitted at a sufficient rate to maintain the engine speed of 900 r.p.m., with light load. On increasing the rate of hydrogen supply and the load, severe knocking occurred, accompanied by occasional induction ignition. Thus the characteristics of hydrogen combustion in an engine as observed by Ricardo, Burstall, and Egerton had been recovered.

Very rich mixtures were then admitted. Combustion was silent and without induction ignition, just as when very weak mixtures were used. This interesting characteristic seems to have been overlooked by earlier experimenters.

It was observed during the experiments mentioned that knock always decreased on retarding ignition, while power increased; this indicated combustion knock rather than detonation knock.

The engine was dismantled for observation of the condition of the combustion chamber surfaces. The piston crown was found to be thickly coated with hard carbon. The piston ring grooves contained granular carbon but the rings were free. The exhaust valve was coated with a greyish white deposit. The inlet valve was fairly clean. The surfaces were thoroughly cleaned and the shrouded inlet valve replaced by a spare exhaust valve of the common tulip shaped type.

First Set of Trials with the Engine Combustion Space Initially Clean. Jacket Temperature, 212° F.; Compression Ratios Rising to 10 : 1, and Arbitrarily Chosen Ignition Timing

Preliminary trials were carried out after warming up the engine by running on leaded gasoline before changing over to hydrogen. There was then no induction ignition at any compression ratio within the range of the engine. Combustion was silent at compression ratios up to 8 : 1 but slight combustion knock occurred at 10 : 1 when using the mixture strength for maximum power. It developed later that ignition had been set too far advanced.

A complete set of trials was then carried out at compression ratios of 4.2, 6.0, 8.0, and 10 : 1 and with the hydrogen-air mixtures varying from very weak to very rich. It was supposed, judging from experiments made by others, that a considerable spark advance would be required for weak mixtures used at low compression ratios and less advance on increasing mixture strength and compression ratio, but nothing definite was known because previously it had not been possible to use anything but weak mixtures at any compression ratio. Trial spark settings of 30°, 20°, 10°, and 0° for the compression ratios mentioned were therefore used.

* The engine was warmed up by running on gasoline in order to save hydrogen.

The experimental results are given by the graphs of Fig. 1; net power output in kilowatts being plotted against rate of hydrogen supply. The values for rate of hydrogen supply are the square roots of pressure differences in inches

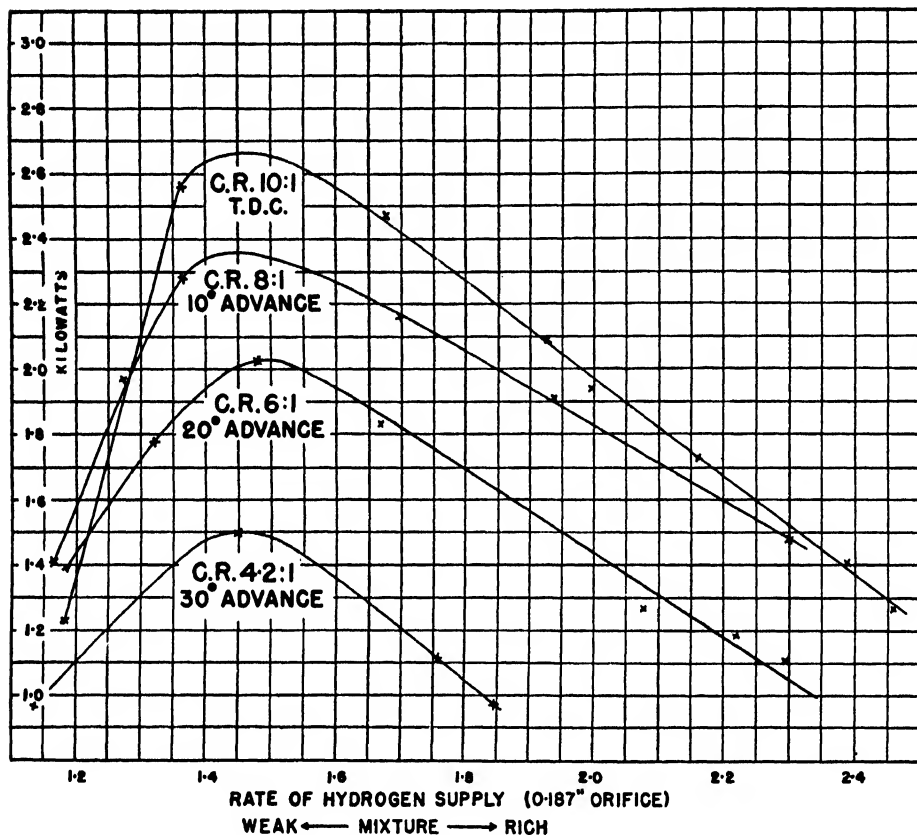


FIG. 1. Relation between power output and mixture strength at compression ratios rising to 10 : 1. Jacket temperature, 212° F.

of water across a circular square edged metering orifice, 0.187 in. diameter, in a thin plate. The graphs are of interest in showing for the first time on record that it is possible to run an engine on hydrogen in any proportion in a mixture with air at compression ratios rising to 10 : 1 and without any combustion difficulty as is evidenced by the consistent variations of power with changes of compression ratio and mixture strength.

Sundry Experiments and Recurrence of Induction Ignition and Knock

Air oscillation in the induction system of the C.F.R. engine is considerable and it appeared that some of the hydrogen supplied at the carburetor throat might accordingly be carried out of the standard inlet pipe to escape into the atmosphere. The standard pipe was therefore replaced by the swirl chamber.

The 0.187 in. diam. orifice for metering the hydrogen was replaced by one of 0.125 in. diam. in order to obtain greater and more easily readable pressure differences, and for further convenience of reading pressure differences the U-tube type of manometer was replaced by one of the single leg variety.

Experiments with hydrogen were resumed on completion of the changes mentioned, after the usual warming up of the engine by running for an hour on leaded gasoline. The earlier combustion difficulties were again encountered and it was impossible to run with the 'correct' mixture strength, even at the low compression ratio of 4 : 1, without violent explosions in the induction system. The difficulties were not overcome by replacing the swirl chamber by the standard inlet pipe, by warming up the engine on unleaded gasoline, or by approaching 'correct' mixture strength from the rich instead of the weak side, or by lowering or raising the jacket temperature, or by taking precautions to avoid electric charges in the induction system possibly due to the high velocity of the mixture passing over sharp edges.

The time of running since the first cleaning was about 12 hr. and the engine was dismantled for inspection of the combustion space and the valves. Both valves were found to have been seating properly and were clean. The exhaust valve showed oxidation colors, brown and red. The piston rings were free but there was some loose carbon in the grooves. The water cooled surfaces were free of loose carbon. The significant finding was a layer of *fluffy carbon*, having the appearance of lamp black, on the piston crown. The combustion chamber, the inlet passageways, and the ring grooves were thoroughly cleaned and the engine reassembled for further trials.

Second Set of Trials, Combustion Space again Initially Clean. Jacket Temperature, 212° F. Air Supply Through Swirl Chamber with Cover Off

The trials were made primarily to verify that the recurrence of combustion difficulties was due to the fluffy carbon mentioned above. They were run at compression ratios of 6, 8, and 10 : 1 and spark setting varied to determine optimum values in varying conditions of mixture strength and compression ratio. There was not a single case of induction ignition in the whole set of trials; combustion was notably quiet except when using the mixture strength for maximum power at a compression ratio of 10 : 1. There was then slight combustion knock.

The experimental results are given by the three sets of graphs of Fig. 2. It is of special interest that maximum power for any but the weakest or richest mixture was obtained when ignition occurred at or very near top dead center. At 10 : 1 compression ratio maximum power was obtained with the spark 5° *retarded*. Regular ignition at this high compression ratio was obtained by reducing the spark gap from the standard setting of 0.025 in. to 0.013 in. Maximum power at 8 : 1 compression ratio was obtained with a spark advance of 5°, whereas at the lower compression ratio of 6 : 1, the optimum setting was at 0°, a somewhat inconsistent result justifying a repetition of the experiments.

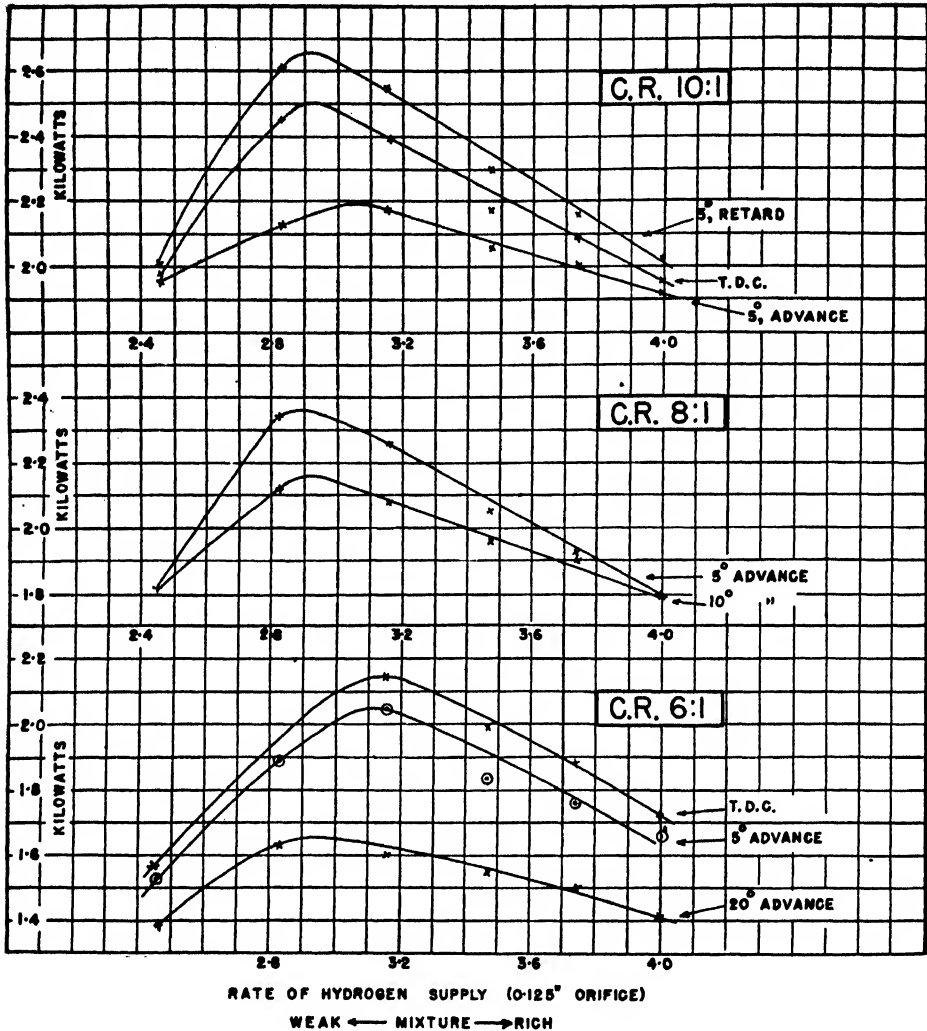


FIG. 2. The effect of ignition timing on power output at compression ratios rising to 10 : 1. Jacket temperature, 212° F.

Routine Cleaning Method

The experiments described above occupied about two hours' running time and no doubt the usual combustion difficulties would have recurred on continued running if no precaution had been taken to maintain the combustion space reasonably clear of fluffy carbon. A routine cleaning method was therefore adopted. Thus, always before starting a day's experiments the bouncing pin and spark plug were removed, the piston moved to top dead center, and the crown cleaned with a tooth brush inserted through the spark plug hole. The engine was then motored round to blow loose carbon through the holes mentioned. As a further precaution to avoid carbon formation by

pyrolysis of hydrocarbon fuel the warming up period on gasoline was reduced to the time required to heat the jacket water to the boiling point and any further warming up done with hydrogen.

The engine was used after the adoption of the cleaning routine for a complete set of trials at low jacket temperature, extended trials using town gas and some sundry experiments made in preparation for future experimental work. There was no recurrence of combustion difficulties.

Third Set of Trials, Routine Cleaning of Combustion Space. Jacket Temperature, 95° to 100° F.

The experiments so far described were made with the standard C.F.R. method of evaporative cooling of the water jackets, that is, jacket water temperature was always 212° F. It is not customary to use such high temperatures in practice and as a matter of interest a set of trials was made with the jackets cooled by tap water, the flow being regulated to maintain an outlet temperature of 95° to 100° F. The standard C.F.R. air inlet pipe was used because it was found during the sundry trials mentioned above that slightly more power was obtained than when using the swirl chamber inlet, no doubt because of the ramming effect of the pipe.

The optimum spark setting for compression ratios of 4, 6, 8, and 10 : 1 was determined for varying mixture strengths. It was found that the optimum setting for the maximum power mixture strength was also the optimum for any richer mixture. But for mixtures on the weak side there would be some advantage in advancing the ignition progressively in accordance with the diminution of hydrogen concentration in the mixture with air.

The trials were made when using the optimum spark setting for the maximum power mixture strength. The experimental results are given by the graphs of Fig. 3. The running of the engine was exceptionally smooth and quiet even when using the mixture strength for maximum power at a compression ratio of 10 : 1.

It will be noted that the graphs are nearly parallel on the rich mixture side but not on the weak side, as would be expected from the finding that the optimum spark advance for the maximum power mixture was also the optimum for richer but not for weaker mixtures.

The Effect of Carbon Nuclei Added to the Hydrogen-Air Mixture

It has been demonstrated by the experiments so far described that induction ignition and combustion knock in the hydrogen engine are due to the igniting action of carbon nuclei derived from the pyrolysis of the lubricating oil. It became of interest, therefore, to observe the effect of carbon nuclei added to the entering gaseous mixture.

The carbon used for the experiments was pulverized charcoal screened with a 200 mesh sieve. It was described as having been activated by heating but had been standing open to the laboratory atmosphere for some weeks before

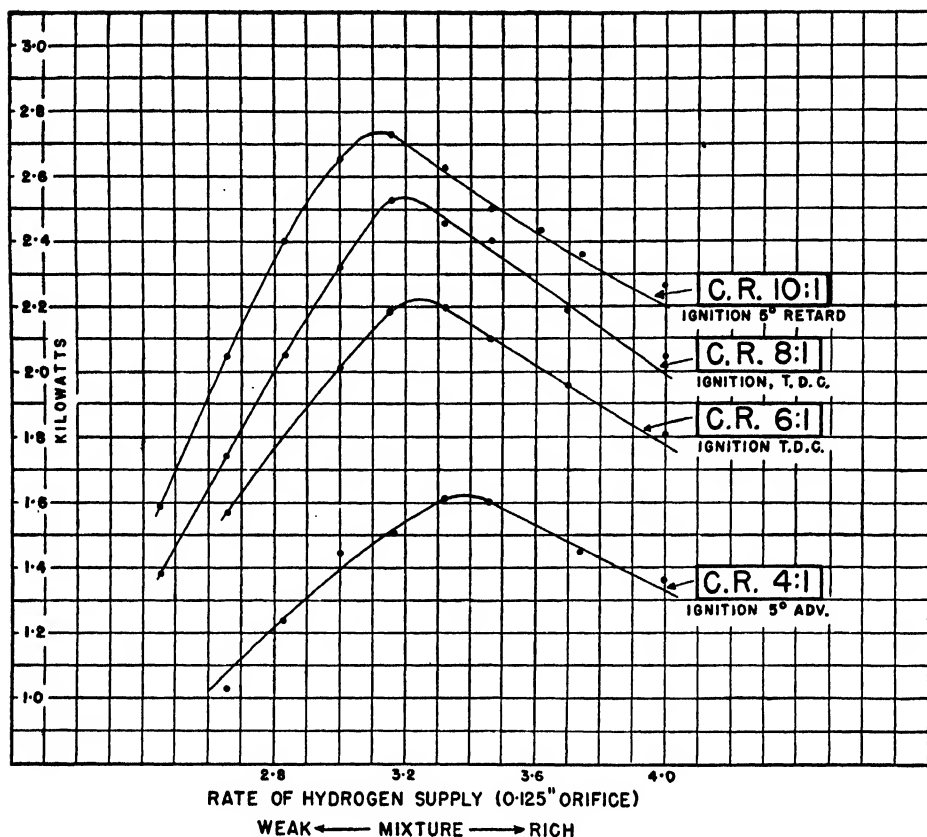


FIG. 3. Relation between power output and mixture strength at compression ratios rising to 10 : 1, nearly optimum ignition timing. Jacket temperature, 95 to 100° F.

being used for the experiments. The carbon was admitted to the air stream in advance of the carburetor throat, at a measured rate, by a device similar to a screw feed coal stoker. The experiment was begun with the combustion space in the condition maintained by the routine cleaning method. The standard pipe inlet was fitted and the jacket water maintained at 212° F. by the standard method.

The engine was started on hydrogen and run at a compression ratio of 6 : 1, with the mixture strength for maximum power and ignition at top dead center. There was no induction ignition, and combustion was silent. The carbon was then admitted at a rate of approximately 2.0 mgm. per stroke. Combustion knock occurred almost immediately and was followed by induction ignition accompanied by explosions in the induction system.

Preparations had been made to carry out a series of experiments to measure the rate of carbon supply required to induce premature ignition and combustion knock or detonation at compression ratios rising to 10 : 1, but, perhaps

as should have been expected, the carbon dust accumulated in the engine to such an extent that induction ignition and combustion knock continued when the supply of carbon to the induction system was shut off.

Indicated Mean Effective Pressure and Indicated Thermal Efficiency

The experiments with the hydrogen engine are regarded as confirming the nuclear theory of ignition. It is of importance, nevertheless, to show that confirmation was obtained while values of the indicated mean effective pressure (I.M.E.P.) and indicated thermal efficiency were such as would be expected from the compression ratios and mixture strengths used during the experiments.

The indicated power was determined by the motoring method. That is, the power required to motor the engine at the experimental speed of 900 r.p.m. was measured immediately after cutting off the fuel supply and added to the net power output measured previously. The method has been widely used by Ricardo and others, and, although it involves the unwarranted assumption that engine friction is of the fluid variety and therefore independent of load, values obtained accordingly are useful for purposes of comparison.

I.M.E.P.—The power required to motor the engine at 900 r.p.m., jacket temperature 212° F., was determined after warming up, using benzene as the fuel, at compression ratios of 6, 8, and 10 : 1. The piston area is 8.28 sq. in., stroke 0.375 ft., and at 900 r.p.m.—

$$\text{I.M.E.P. (lb. per sq. in.)} = \text{Indicated horse power} \times 23.6.$$

Maximum power output being taken from the graphs of Fig. 2, the data given in Table I are obtained.

TABLE I

INDICATED MEAN EFFECTIVE PRESSURES AT COMPRESSION RATIOS OF 6, 8, AND 10 : 1,
WHEN USING THE MAXIMUM POWER MIXTURE STRENGTH

Compression ratio	Net output, kw.	Motoring power, kw.	I.H.P.	I.M.E.P., lb./sq. in.
10 : 1	2.66	1.61	5.73	136
8 : 1	2.36	1.59	5.30	125
6 : 1	2.15	1.48	4.87	103

Indicated Thermal Efficiency.—Relative rates of hydrogen supply are reasonably accurate but approximate values only of quantities were obtained, the metering orifice not having been calibrated. Thermal efficiencies calculated accordingly, again using data from Fig. 2, are given in Table II.

TABLE II

INDICATED THERMAL EFFICIENCIES; COMPRESSION RATIO, 10 : 1

Mixture strength	Net power, kw.	Indicated power, kw.	I.H.P.	Indicated thermal efficiency, %
15% rich	2.40	4.01	5.38	34.2
3% rich	2.64	4.25	5.70	39.8
Max. power	2.66	4.27	5.78	41.2
5% weak	2.58	4.19	5.62	42.4
17% weak	2.02	3.63	4.87	42.0

It will be noted from Table II that maximum efficiency was obtained for the mixture strength giving somewhat less than maximum power, as would be expected.

Section II

Discussion of Experimental Results

Induction ignition, normally described as "firing back through the carburetor", was obtained when, starting with a clean engine, sufficient time elapsed for an accumulation of fluffy carbon in the combustion space. The effect was not obtained if accumulation of the carbon were prevented. It is concluded that ignition of the fresh charge when obtained was due to glowing particles of carbon present in the residual charge.

Ignition by sudden compression.—The absence of the effect when the engine combustion space was nearly free of fluffy carbon is of interest in respect of experiments by others on the ignition of electrolytic gas ($2\text{H}_2 + \text{O}_2$) and hydrogen-air mixtures by sudden compression. Falk (5,6) concluded that the presence of lubricant (lanoline) was without effect on ignition temperature, but the experiments of Dixon, Bradshaw, and Campbell (2) and Dixon and Crofts (3) demonstrated that consistent ignition temperatures could be obtained solely when the lubricant was present as an extremely thin film on the surface of the combustion space, a condition set by the vacuum method of filling the space with the combustible mixture. Tizard (14), using the Ricardo compression ignition machine, similar to an engine cylinder, could not avoid the presence of a thin film of lubricant on surfaces exposed to the temperatures of compression and obtained ignition temperatures accordingly. When the Ricardo machine was redesigned to permit compression of the combustible mixture in a cylinder supposed to be free of lubricant, Tizard and Pye (15) were unable to obtain consistent ignition temperatures. Fenning (8), on continuing experiments with the machine, found that lubricant did in fact penetrate into the compression cylinder in an irregular manner. Thus, out of five compressions with a compression ratio of 9.2 : 1 and a jacket temperature of 97°C ., two compressions resulted in premature ignition, two caused ignition after delay periods of 0.009 and 0.015 sec. and a fifth failed to cause ignition.

Nevertheless, when using the hydrogen engine at 10 : 1 compression ratio, a jacket temperature of 100° C. and more nearly adiabatic compression, the mixture failed to ignite prior to passage of the spark, if the combustion space were nearly free of finely divided carbon. That is, ignition did not occur in the body of the gaseous mixture in the absence of material nuclei of ignition as would be expected from the experiments of King (9) and King and Mole (11).

Flame velocity.—It is generally agreed that maximum engine power is obtained when maximum combustion pressure occurs about 12° after top dead center. It will be seen from Figs. 2 and 3 that at 10 : 1 compression ratio maximum power was obtained when the spark passed at 5° after top dead center. Combustion was thus completed in about 7° of crank angle, that is in 0.0013 sec., engine speed being 900 r.p.m. The flame would have traveled a distance equal to the diameter of the cylinder, 3.25 in., so velocity must have been approximately 63 m. per sec. even with no allowance for the time interval between passing the spark and the start of pressure rise. Flame velocity in the nearly clean combustion space of the engine is comparable with that observed by Fenning (7) when similar mixtures in a clean bomb were ignited by a spark, if allowance be made for differences in dimensions, initial temperature, and pressure. The flame velocity attained in the engine or bomb did not approach that of true detonation and in neither case was there any evidence of that phenomenon.

The pro-knock effect of carbon nuclei.—When hydrocarbon fuels, especially paraffins, are used in an engine, finely divided carbon can be derived from pyrolysis of the fuel, and maximum concentration occurs necessarily in the end gas [Part IV (10)]. Self-ignition can occur accordingly and nearly simultaneously throughout the mass of the gas; this results in detonation knock.

When hydrogen is used as the fuel, finely divided carbon can be obtained from the lubricating oil only and must be distributed by turbulence, more or less uniformly. There can be no preferential concentration in the end gas, consequently the sole effect of the carbon, after the passage of the spark, is to increase flame velocity and thereby promote combustion knock, an effect similar to that obtained by Fenning (7) on igniting electrolytic gas when the time from the passage of the spark to the attainment of maximum pressure was as short as 0.00072 sec., that is, combustion knock was obtained in the bomb on increasing flame speed by using electrolytic gas and in the engine by impregnating hydrogen-air mixtures with finely divided carbon.

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COPPER CORROSION AND ITS CONTROL IN STARCH SYRUP MANUFACTURE¹

BY K. A. CLENDENNING²

Abstract

Contamination of starch syrups with copper was kept to a minimum by mixing the acid catalyst with the starch slurry rather than with the priming water. Copper removal at the neutralization stage was promoted by protein impurities in the converted starch, high pH, and hot filtration. Decolorization with activated carbon removed less than 20% of residual copper, whereas acid-tempered bone char removed over 99%. The copper content of dilute syrups was determined without preparatory ashing by precipitation with salicylaldoxime.

Introduction

Little information has appeared in the literature concerning the corrosion of copper converters as a problem in starch syrup production. In view of the importance of the product as a foodstuff, consideration of the factors influencing both the introduction and removal of copper at successive stages of its manufacture appears desirable.

The present report deals with the protective action of starch hydrolysis products towards copper, the influence of protein content, level of pH adjustment, and filtration temperature on the removal of dissolved copper at the neutralization stage, and the relative effectiveness of bone char and activated carbon decolorization treatments in removing copper from the neutralized liquor. An adaptation of Riley's salicylaldoxime procedure for copper (15) was employed in this study, which permitted determination of the copper content of dilute syrups without preparatory ashing.

Copper and copper-containing alloys are quite resistant to dilute hydrochloric acid in the absence of oxygen and oxidizing constituents (9, p. 2; 17, p. 225). Oxygen is introduced with each batch of slurry, and it is known to stimulate copper corrosion by acid liquors (9, p. 2; 17, p. 225). The contents of the partially filled converter are highly acidic when the catalyst is mixed with the priming water, as recommended by many authors (1, pp. 181-187; 12, p. 215; 13; 18). A uniformly low acidity, on the other hand, is maintained during the filling operation by mixing the acid with the cold starch slurry before it enters the converter (4; 10, p. 284; 19).

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Steam is blown into the converter contents throughout the filling operation, and, with thorough sparging, oxygen introduced with the priming water and slurry should be swept out before the pressure is raised. These considerations indicate that contamination of starch hydrolyzates with copper largely originates in the filling operation, and that it is promoted by introducing the acid with the priming water. Its dependence on the period of service of individual converters is also noteworthy; the experience of the industry has been that the copper content of successive hydrolyzates gradually diminishes, evidently through deposition of a protective coating of reversion products on the exposed metal surface.

Published information on the removal of dissolved copper from starch hydrolyzates is limited to that provided by McLachlan (11). According to this author, neutralization with sodium carbonate removes most of the dissolved copper, and copper precipitation from corn starch hydrolyzates is maximal at pH 5.1. He also reported less complete removal of copper by sodium carbonate precipitation from starch hydrolyzates than from solutions of copper in distilled water. The method used in determining copper in this work was not disclosed, and determination of pH by titration is unsatisfactory by present standards. It appeared necessary, therefore, to repeat McLachlan's work, as well as to investigate other aspects suggested by his published findings.

Copper Determination

A method for the determination of copper in dilute starch syrup was sought that did not require preparatory ashing. Color development in the presence of excess ammonia, as well as precipitation as copper thiocyanate (5, p. 200) proved quite unsatisfactory at low copper concentrations even in the absence of organic matter. Reif's microgravimetric method (14), in which salicylaldoxime is employed as precipitant, could not be used without modification over the greater part of the concentration range for which it was stated to be applicable.

Addition of excess salicylaldoxime reagent, as directed by Riley (15), to solutions containing less than 40 mgm. copper per liter resulted in turbidity, the intensity of which varied with the copper content. Flocculation occurred on standing with occasional agitation, and after 24 hr. in flowing tap water the supernatant liquid was rendered perfectly clear by precipitation, even at copper contents of 2 mgm. per liter. With this extension of time between addition of the precipitant and filtration, Riley's procedure gave quantitative recoveries from solutions of copper in distilled water at much lower copper concentrations than those that have previously been reported (Table I). Quantitative recoveries of copper were similarly obtained from 16° Bé. starch hydrolyzates of low copper content.

Completeness of precipitation was checked in routine applications with additional salicylaldoxime. Adequacy of washing the copper salicylaldoxime precipitate was established by re-extraction, drying, and weighing. In the

present applications, inorganic constituents were limited to sodium chloride, cupric chloride, and trace contaminants introduced with the starch. Previous work has shown that interference from these sources may be safely neglected

TABLE I

RECOVERY OF COPPER FROM DISTILLED WATER AND FROM STARCH SYRUP BY THE RILEY PROCEDURE, AFTER A ONE-DAY INTERVAL BETWEEN ADDITION OF PRECIPITANT AND FILTRATION

(Mgm. per liter)

Copper present	Distilled water, copper found	16° Bé. syrup, copper found
100.0	100.8	99.6
80.0	80.0	80.1
60.0	59.4	58.0
40.0	39.0	40.0
20.0	20.2	20.0
16.0	—	16.3
12.0	—	13.0
10.0	10.4	—
8.0	—	8.6
4.0	—	4.2

(7, p. 114). It was concluded that interference from nitrogenous impurities in the acidified salicylaldehyde medium could also be neglected, since no precipitation occurred in blank determinations on neutralized and filtered 16° Bé. starch hydrolyzates to which copper had not been added. The chief limitation of the method apparently is the error in weighing the precipitates when the copper concentration is below 10 p.p.m.

Results

Inhibition of Copper Corrosion by Starch Syrup

Table II provides data on copper corrosion by aqueous solutions at pH 1.8 and higher levels in the presence and absence of 16° Bé. starch syrup. The dilute starch syrup had a protective action at all pH levels, its reducing action evidently counteracting the known stimulating effects of oxygen. These results indicate that the rate at which traces of copper are brought into solution diminishes with the progress of individual conversions.

Inhibition of Gelatinization by Dilute Acid

Corrosion of new copper converters during the filling operation may be greatly reduced by mixing the acid catalyst with the slurry rather than the priming water. The feasibility of this practice depends largely on the type of holding tanks that are employed—if these are metallic, contamination of the product may then result from slurry acidification. Assurance is also needed that acidification does not promote slurry gelatinization.

TABLE II

CORROSION OF COPPER BY 16 BÉ. STARCH SYRUP AND BY WATER ADJUSTED TO DIFFERENT pH LEVELS WITH HYDROCHLORIC ACID

(After 16 hr. contact at 100° C.)

pH	Sample	Wt. loss of copper test plates, mgm. per sq. dm.	Appearance of test plates
1.8	Water	306.0	Badly pitted and blackened
	Syrup	13.2	Tarnished
4.8	Water	15.6	Tarnished
	Syrup	8.8	Slightly tarnished
7.0	Water	11.4	Tarnished
	Syrup	8.2	Slightly tarnished

The data of Table III were obtained by microscopic observation of 0.8% starch slurries at 1° C. temperature intervals. Hydrochloric acid even at one-tenth normality raised the temperature at which marked swelling occurred

TABLE III

INHIBITION OF STARCH GELATINIZATION (GRANULE SWELLING) BY DILUTE HYDROCHLORIC ACID

HCl normality	pH	Gelatinization temperature, °C.					
		Wheat starch		Corn starch		Potato starch	
		Incipient	All large granules swollen	Incipient	All large granules swollen	Incipient	All large granules swollen
0	6.5	55	59	61	70	55	63
0.005	2.35	55	59	62	70	55	63
0.02	1.80	55	62	63	71	55	65
0.10	1.12	56	64	64	72	56	65

in all three types of starch. These observations are in agreement with those of Samec (16, p. 177), who reported increases in the gelatinization point of starch in dilute sulphuric and hydrochloric acid solutions: it was only with concentrations above 5 *N* with sulphuric and 1 *N* with hydrochloric acid that the gelatinization point dropped below that shown in water; acetic acid, on the other hand, decreased the gelatinization point at the lowest concentrations tested. This effect of acid has received little attention; it is a matter of interest that the catalyst of starch hydrolysis should inhibit the first stage of granule disintegration.

Factors Influencing the Removal of Dispersed Copper at the Neutralization Stage

* The data of Table IV were obtained by adjusting an aqueous cupric chloride solution containing 200 p.p.m. copper to a pH of 1.8 with hydrochloric acid.

TABLE IV

INFLUENCE OF pH ADJUSTMENT WITH SODIUM CARBONATE AND OF FILTRATION TEMPERATURE ON THE PRECIPITATION OF COPPER CHLORIDE FROM AQUEOUS SOLUTION

pH	Filtration temperature, °C.	Filtrate copper content, mgm. per liter	Precipitation of copper, %
1.8 - 5.4	80	200	Nil
	25	200	Nil
5.85	80	90.7	54.7
	25	111.9	44.1
6.25	80	10.8	94.6
	25	33.0	83.5
7.00	80	3.6	98.2
	25	9.1	95.0
8.00	80	6.0	97.0

Sodium carbonate was then added to provide successively higher pH levels with accompanying precipitation of copper. Following filtration through Whatman No. 42 at 80° and 25° C., the filtrates were analyzed.

No precipitate was formed until the pH was brought above 5.4. The bulk of the copper was precipitated between a pH of 5.85 and 7.0, but it was not removed completely even at pH 8.0. Copper removal was consistently higher with hot as opposed to room temperature filtration. Judging from the observations of Hopkins and Beebe (8), and of Cloutier, Pelletier, and Gagnon (3), the copper precipitate is a basic complex with considerable affinity for water. With rising temperature, this unstable complex is rendered less soluble.

The experiments reported in Table V differed from the foregoing in that distilled water was replaced with (a) finished potato syrup diluted back to 16° Bé. and acidified, (b) freshly prepared 16° Bé. potato, and (c) wheat starch hydrolyzates. These solutions, which were prepared in glass-lined equipment (2), permitted observations to be made on the precipitation of copper by neutralization of starch hydrolyzates containing 0.007, 0.03, and 0.1% nitrogen respectively, expressed as protein on a wet basis. Prior to neutralization and filtration, 200 mgm. copper per liter was provided by the addition of cupric chloride.

Consistently less copper was removed from the diluted starch syrup at and above a pH of 6.0 than from distilled water. Copper precipitation was shown at a pH of 5.0 from the diluted starch syrup—below the point at which preci-

pitiation began from aqueous cupric chloride solution. Copper removal was higher at all pH levels from freshly prepared potato starch hydrolyzate than from finished syrup diluted back to 16° Bé. Copper removal from the wheat

TABLE V

INFLUENCE OF pH ADJUSTMENT AND PROTEIN CONTENT ON THE PRECIPITATION OF COPPER FROM 16° BÉ. STARCH HYDROLYZATES

(Initial copper content, 200 mg. per liter)

pH	Copper removal, %		
	Finished potato syrup diluted to 16° Bé.	Potato starch hydrolyzate	Wheat starch hydrolyzate
4.0	0	32.6	63.0
5.0	24.8	51.5	85.0
6.0	36.7	81.2	92.0
7.0	89.0	94.8	72.5
8.0	91.3	96.1	45.9

starch hydrolyzate differed from that from all other solutions tested in that a maximum was shown at intermediate pH levels, as was reported for corn starch hydrolyzates by McLachlan (11). The protein impurities in wheat starch promoted copper removal with pH adjustments to 4.0–6.0, and hindered copper removal at and above neutrality.

The amounts of copper removed on adjusting to pH 5.0 are of greatest practical interest since this pH appears to be generally suitable as a neutralization point in starch syrup production. The removal of dissolved copper that was observed with filtration at 80° C. for this pH level showed important changes with the nature of the medium: from water, 0%; diluted starch syrup, 25%; potato starch hydrolyzate, 51.5%; and wheat starch hydrolyzate, 85%. The different solutions appeared in the same order with respect to copper removal at pH 4.0 and 6.0. At pH 7.0 and 8.0 less copper was precipitated from the wheat starch hydrolyzate than from any other solution tested.

To determine completeness of copper removal at a lower copper concentration, wheat starch hydrolyzate was adjusted to a copper content of 20 mgm. per liter. After neutralization to pH 5.0, decolorization by contact for one hour with 1% activated carbon on the juice weight and filtration at 80° C., the filtrate copper content was 4 mgm. per liter, representing 80% removal.

Removal of Residual Copper with Bone Char vs. Activated Carbon

Hinze (6) objected to the substitution of activated carbon for bone char decolorization of starch syrup because of its lesser ability to remove undesirable metallic salts. To test the efficiency of these decolorizing agents with respect to copper removal, cupric chloride was added to neutralized and filtered

16° Bé. wheat starch hydrolyzates (pH 5.0, D.E. 50) to provide a copper content of 200 p.p.m. Samples of the dilute syrup were then mixed with activated carbon and acid-tempered bone char in proportions approximating those employed for decolorization (1% and 50% of the syrup weight respectively). After one hour at 80° C. the syrups were filtered and analyzed. Copper removal exceeded 99% with bone char, and the filtrates were water white and free of metallic taste. Approximately 17% removal was shown with activated carbon, and the thin syrup was light green and unpalatable. Under conditions favoring a high content of residual copper, bone char is superior to activated carbon as a refining agent.

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PRODUCTION OF SYRUPS FROM WHEAT, POTATO, TAPIOCA, AND WAXY CEREAL STARCHES¹

By K. A. CLENDENNING² AND D. E. WRIGHT³

Abstract

Syrups prepared in semipilot plant equipment from wheat, corn, waxy corn, tapioca, and potato starches of low protein content were almost identical in taste and appearance. Differences in nature and amount of non-carbohydrate constituents did not necessitate modifications of the process. Wheat, corn, and waxy corn slurries hydrolyzed at approximately the same rate with 0.2% hydrochloric acid whereas potato starch hydrolyzed less rapidly. Contamination with 1.6% protein did not depress the hydrolysis rate but promoted foaming, turbidity, and bitterness. Loss of insoluble solids on the filter press averaged 1.25% for cereal and 0.3% for potato starch hydrolyzates. Complete decolorization of 14° and 30° Bé. syrup was effected by 0.5% activated carbon, based on the juice weight at each stage. Tap water promoted color development in the evaporator and inhibited color removal by active carbon. Color and fluorescence development in stored syrups was promoted by protein impurities, light, and tap water, and was strongly inhibited by sodium bisulphite. Syrups that remained colorless almost indefinitely were prepared from prime quality starches by using distilled water in the process and either acid-extracted carbon or bone char as decolorizing agents.

Introduction

The recent shortage of sucrose opened an unusually large market for starch syrup as an alternative sweetening agent. Supplies of raw material and the capacities of existing plants did not permit a large increase in the domestic production of corn syrup. As a result, corn syrup was imported from the U.S.A., Mexico, and Argentina, and commercial production of syrup from wheat and potatoes was undertaken in Canada for the first time.

These circumstances gave considerable impetus to studies of wheat starch manufacture, and several processes have now been described that provide starch of low protein content in high yield on a pilot plant scale (7, 10, 13, 14). The quality of commercial wheat syrups of both Canadian and American origin, however, has remained inferior to that of corn and potato syrups (6). Most of the wheat syrups examined by the authors were dark and became increasingly turbid during storage. Chemical analysis of these products indicated that the starches employed were heavily contaminated with protein, and that excessive amounts of sodium chloride and other salts were introduced in their manufacture (6).

The purpose of the present investigation was the provision of detailed information on the production of syrups from different types of starch by the batch acid hydrolysis process. The starches of wheat and potatoes received particular attention because of recurring surpluses in these products and their

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recent use in syrup production. Tapioca starch was included because it usually is the least expensive starch on the world market. A comparison of ordinary and waxy corn starches was also judged of interest, since it permitted demonstration of the behavior of the amylopectin or branched component in the conventional conversion process.

Materials and Methods

The starches employed in this study were chiefly those whose composition and source are shown in Table I. Wheat starch slurries prepared from patent flour by the screening process described by Shewfelt and Adams (13), and

TABLE I
SOURCE AND COMPOSITION OF STARCHES

Starch	Source	Moisture, %	Ash, % d.s.	Fat, % d.s.	Protein, % d.s.
Wheat	Stein Hall and Co., New York, N.Y.	11.09	0.26	0.63	0.38
Wheat	N.R.C. pilot plant	10.83	0.12	0.60	0.34
Corn	Canada Starch Co., Cardinal, Ont.	10.48	0.05	0.64	0.32
Waxy corn	American Maize Products, Roby, Ind.	10.24	0.05	0.20	0.26
Potato	F. W. Pirie Co. Ltd., Grand Falls, N.B.	13.05	0.32	0.12	0.11
Tapioca	Stein Hall and Co., New York, N.Y.	10.17	0.08	0.27	0.14

concentrated to 16° Bé. by overnight settling, were also employed without further purification. To test the effects of protein contamination directly, prime quality wheat starch was blended with 100 mesh 'vital gluten'* and with patent flour to provide protein contents of 0.4, 0.8, and 1.6%. No attempt was made to exclude mineral impurities by the use of 'acid' starches since laboratory tests indicated that most of the bound acid was liberated as the starch disintegrated. As the various starches differed in acid-binding power, preparatory treatment with acid could lead to differences in free acid as hydrolysis progressed.

The extremely high viscosity of 23° Bé. waxy corn starch slurries at room temperature made it impossible to feed suspensions of this density to the converter. Conversion experiments on this starch were accordingly limited to 19° Bé. and lighter densities. Microscopic examination of the waxy starch revealed no evidence of incipient gelatinization or of gelatinous impurities, and nitrogen and pentosan determinations showed close agreement between the ordinary and waxy corn starch samples. Dilatancy tests also failed to reveal any distinction. The stiffness of the 23° Bé. waxy starch slurries may have resulted from granule adherence, of which there was some evidence in micromanipulation tests.

* Supplied by Wheat Industries Ltd., Enfield, N.S.W., Australia.

Dextrose equivalents and dextrose contents of the starch hydrolyzates were determined by the Shaffer-Hartmann and Sichert-Bleyer methods respectively, as modified by Zerban and Sattler (16). Optical rotatory power was determined at 20° C. on 100 ml. solutions containing 26 gm. solids and was expressed as specific rotation on a total solids basis. Slurry and syrup density measurements were made at 25° and 60° C. respectively with stream-lined C.I.R.F. hydrometers*. Color was determined by transmittance measurements with the Evelyn colorimeter (Wratten filter 420) using colorless syrup of corresponding dextrose equivalent and density in setting the galvanometer (6). Fluorescence was determined by the method outlined by Pearce and Thistle (12). Moisture was determined by drying *in vacuo* on Filter-cel as directed by Cleland and Fetzer (4). Further details concerning the analytical methods employed are presented elsewhere (6).

It was found necessary to extract fresh bone char exhaustively with dilute hydrochloric acid before use on starch hydrolyzates: decolorization otherwise was very slow, and the decolorized syrup became very dark during evaporation. Three two-hour extractions with fresh lots of boiling 0.5 *N* hydrochloric acid followed by extraction with distilled water until the wash liquid remained neutral proved satisfactory and was adopted as a laboratory 'acid-tempering' treatment. This raised the carbon content from 8-9%, the usual level for sucrose refining, to 20-25%.

The processing equipment consisted of gravity filters, filter press, converter, slurry tank, and vacuum evaporator (Fig. 1). The bone char filters were constructed and operated in accordance with commercial practice. The glass-lined converter was equipped with steam jacket, steam sparger, and mechanical agitator. Ports were provided at the top for pressure gauges, thermometer well, sampling tube, air outlet, and slurry inlet, and a large gate-valve outlet at the bottom allowed rapid removal of the hydrolyzed liquid. A 5 gal. vessel equipped with an agitator was located above the converter, and the starch suspension was fed from it by gravity in filling the converter. Five-gallon earthenware crocks served as neutralizing vessels. The filter press was of standard 6 in. plate and frame construction. The evaporator consisted of a steam-jacketed copper kettle, of 5 gal. capacity, condenser, receiver, and vacuum pump.

It has been found most economical in the syrup industry to employ starch slurries having a density only slightly below the limit imposed by dilatancy, i.e., 22° to 24° Bé. The tendency of such heavy suspensions to form massive lumps when heated and the high viscosity and poor heat transfer properties of the paste necessitate special precautions in filling the converter. Even with starch of the highest quality, improper technique at this stage leads to off-flavor and aftertaste. The method of adding the hydrochloric acid is also important (5); with the present glass-lined equipment it was most conveniently introduced with the priming water. A concentration of 0.2%

* Obtained from Wm. Hiergesell and Sons, 295 Pearl St., New York 7, N. Y.

PLATE I

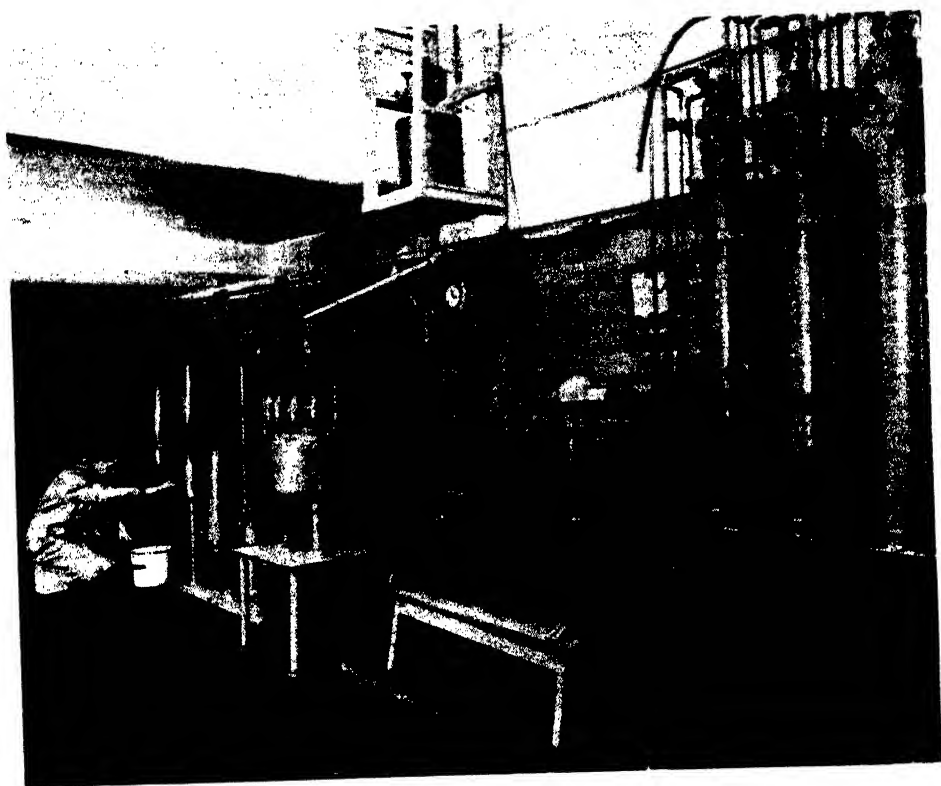


FIG. 1. *General view of the equipment.*

hydrochloric acid, based on the dry weight of starch, provides adequate acidification for 22° to 24° Bé. slurries, and this concentration was adopted as a standard condition. This method of expressing the acidity ensures uniformity in the sodium chloride content of the product when slurries of fluctuating starch content are employed.

At the outset of each conversion, sufficient 'priming' water is placed in the empty converter to cover the open-type steam coil: with converters of 2000 gal. capacity, approximately 100 gal. of water is required for this purpose. The water is brought to boiling by steam injection before addition of the 22° to 24° Bé. starch slurry is begun. During the filling operation, which must proceed continuously, slurry addition and steam injection are integrated so that boiling of the converter contents proceeds vigorously, with steam escaping freely from the air vent.

After the converter has been filled and swept out thoroughly with steam, the pressure is raised to approximately 35 p.s.i. The progress of each conversion must be followed by iodine tests because of the magnitude of interbatch differences in hydrolysis rate. Ten drops of iodine reagent (1 gm. iodine and 2 gm. potassium iodide in 250 cc. water) are added to a test tube containing 10 to 15 cc. of the cooled hydrolyzate. Shaking to distribute the iodine through the upper half of the sample provides maximum definition of color. It is particularly helpful to have reference samples on hand for the range 30 to 40 D.E. Iodine should be added periodically to fresh samples of the reference hydrolyzates for accurate comparisons. Hydrolyzates that were removed immediately after the disappearance of mauve coloration showed dextrose equivalent values of 38 to 42 D.E. with the present equipment, irrespective of starch type and purity. Two additional minutes at 35 p.s.i. provided hydrolyzates having D.E. values of 45 to 50. A D.E. value of 55 is regarded as the upper limit for the acid hydrolysis process because of the off-flavor and crystallization tendency of more completely hydrolyzed products.

The bulk of the sodium carbonate required for neutralization is added with continuous agitation as rapidly as the foaming tendency will permit. Gradual additions are then made, with periodic pH measurements, until a value of 5.0 to 5.1 is attained. In industrial practice, fatty impurities are removed in skimming tanks as described by Bartling (3). Hyflo Super Cel (0.1 to 0.2%, based on the liquid weight) is added to facilitate removal of flocculated proteins and other impurities on the filter press. Activated carbon (0.2 to 0.5%, based on the liquid weight) may be introduced with the filter aid either before or after neutralization, or may be added to the hydrolyzate after the bulk of the insoluble impurities have been removed by filtration. The carbon is removed on the filter press after approximately 20 min. contact at 80° C. Evaporation to 30° Bé. may be effected *in vacuo* or at atmospheric pressure. A further 20 min. treatment at 80° C. with 0.5% activated carbon and 0.1% Hyflo Super Cel on the 30° Bé. syrup weight removes the color developed during the first evaporation. The final filtration at this density must effect complete

removal of suspended impurities. In evaporating the heavy syrup *in vacuo* to the final density of 42° to 43° Bé., control Beaumé measurements are most conveniently taken at the evaporation temperature of 140° F., a correction of 1.0° Bé. being added to obtain the conventional density value at 100° F. (9).

In decolorizing with bone char, the neutralized hydrolyzate is defatted and is freed of flocculated proteins by filtration with diatomaceous earth before being percolated through the gravity filters. After evaporation to 30° Bé., the syrup is again decolorized with bone char, and filtered if necessary before its evaporation to final consistency.

Results and Discussion

Hydrolysis

Successive batches of 23° Bé. slurries converted at 35 p.s.i. with 0.2% hydrochloric acid showed large differences in hydrolysis rate (Table II).

TABLE II

EFFECT OF SLURRY DENSITY ON THE REPRODUCIBILITY OF WHEAT STARCH HYDROLYSIS AT 35 P.S.I. WITH 0.2% HYDROCHLORIC ACID, D.S. BASIS

Conversion time, min.	Slurry density, °Bé.		
	23	18	12
	Mean dextrose equivalent of hydrolyzates, d. s. basis		
25	42.7	42.9	31.5
35	54.8	55.0	39.9
45	64.2	63.9	43.1
S.D.	3.8	3.8	1.3

With heating periods of 25 to 45 min., the standard error for 18 conversions was 3.76 dextrose equivalent units. These differences were observed with wheat starch from a uniform lot after careful standardization of the filling operation, as well as of the conversion treatment at elevated pressure. Batch differences of similar magnitude were also observed with other types of starch. Reproducibility and rate of hydrolysis were not affected significantly by mixing the hydrochloric acid with the starch slurry rather than the priming water. Reproducibility was improved and the hydrolysis rate was diminished on reducing the slurry density to 12° Bé., the acid concentration being maintained at 0.2% of the solids content (Table II). The heterogeneity and poor heat transfer properties of the reaction mixture evidently are responsible for the differences in hydrolysis rate observed between successive batches at high starch concentrations and for the existing lack of critical data on starch hydrolysis under these conditions. These characteristics also are the principal obstacles that must be surmounted in the development of continuous conversion processes (11).

The crude wheat starch slurries obtained by the screening process (13) deposit solids slowly, and, as a result, the slurries that have been employed on an industrial scale have usually been of low and variable density. Table III

TABLE III

EFFECTS OF STARCH AND ACID CONCENTRATION ON THE HYDROLYSIS OF WHEAT STARCH

Conversion time, min.	Acid conc'n.	Slurry density, °Bé.		
		23	18	12
		Dextrose equivalent values of hydrolyzates		
25	0.2%, d.s.	29.0	43.0	31.5
	0.015 <i>N</i>	29.0	46.1	71.7
35	0.2%, d.s.	43.7	55.0	39.2
	0.015 <i>N</i>	43.7	59.8	77.4
45	0.2%, d.s.	60.9	63.8	46.4
	0.015 <i>N</i>	60.9	72.2	79.2

demonstrates important effects of slurry density on the rate of hydrolysis. Rate of hydrolysis increases with decreasing slurry density when the amount of acid is maintained constant on a volumetric basis, and decreases when the acid is maintained at a constant percentage of the dry weight of starch. Use of dilute starch slurries necessitates hydrochloric acid concentrations in excess of 0.2% if the desired conversion is to be effected rapidly. The high sodium chloride content of many of the commercial wheat syrups examined by us (6) is attributed to this circumstance.

The lack of agreement between successive conversions on the same starch makes it impossible to provide satisfactory reference data for the hydrolysis of different starches under the usual conditions of syrup production. The data of Table IV indicate, however, that potato starch is more resistant to acid hydrolysis than tapioca or cereal starches. The tapioca syrups showed higher specific rotation values and lower dextrose contents than were observed with other starch hydrolyzates at similar dextrose equivalent levels.

With 23° Bé. slurries, the iodine end points were attained after 25 to 30 min. at 35 p.s.i. with the tapioca and non-waxy cereal starches, and after 35 to 40 min. with potato starch. The greater resistance to hydrolysis of potato starch was again apparent in experiments on 12° Bé. slurries (Fig. 2). Potato starch also shows greater acid-binding power, which Smirnov (15) has attributed to esterified phosphate in the amylopectin fraction. The concordance of the waxy and ordinary corn starch data indicates that absence of the amylose fraction has little effect either on the rate of reducing sugar formation, or on the composition of the product.

TABLE IV

ANALYTICAL DATA FOR HYDROLYZATES OF WHEAT, CORN, WAXY CORN, TAPIOCA, AND POTATO STARCHES PREPARED WITH 0.015 *N* HYDROCHLORIC ACID AT 35 P.S.I.

		Conversion time, min.				
		20	25	30	35	40
Corn 23° Bé.	D.E.	31.2	48.0	56.5	62.3	67.0
	glucose	13.5	30.7	36.7	44.5	50.5
	$[\alpha]_D^{20}$	—	137.9	123.2	110.5	101.9
Corn 19° Bé.	D.E.	36.3	44.2	50.6	56.3	61.1
	glucose	21.4	28.3	33.4	37.2	42.9
	$[\alpha]_D^{20}$	—	144.2	134.8	124.4	117.7
Waxy corn 19° Bé.	D.E.	26.7	36.8	44.1	50.9	56.1
	glucose	14.3	21.0	28.0	31.5	38.0
	$[\alpha]_D^{20}$	—	157.5	138.4	136.6	125.5
Wheat 23° Bé.	D.E.	29.0	38.7	43.7	48.3	55.8
	glucose	13.5	20.2	23.0	29.1	37.0
	$[\alpha]_D^{20}$	—	147.7	137.8	127.7	117.3
Potato 23° Bé.	D.E.	23.5	31.1	37.4	42.6	46.4
	glucose	12.8	15.9	20.8	25.0	28.2
	$[\alpha]_D^{20}$	—	168.4	156.9	149.6	140.1
Tapioca 23° Bé.	D.E.	37.1	40.0	47.1	52.8	58.0
	glucose	13.7	16.6	22.0	25.5	32.6
	$[\alpha]_D^{20}$	179.6	174.8	167.2	158.2	150.0

Commercial wheat syrups of high protein content showed high sodium chloride contents (6), which might suggest that the protein impurities necessitated the use of additional hydrochloric acid. Table V shows that the hydrolysis rate under pressure was not reduced by the presence of 1.6% protein. The time required in reaching the iodine end point also was within the usual 25 to 30 min. range. It is therefore unnecessary to increase the acidity with this degree of protein contamination, which is far above the level at which syrup free of off-flavor can be obtained.

Syrups prepared from starches that were heavily contaminated with protein were consistently objectionable in taste and appearance. Bitterness and aftertaste were not removed by repeated passage through the bone char filters. Nitrogenous impurities cause troublesome frothing in the evaporator and affect the usefulness of the syrup in the confectionery and soft drink trades. Considerable haze also develops in finished syrups of high nitrogen content. When protein impurities are responsible, the latter fault can largely be corrected by diluting to 25–30° Bé., filtering off the flocculated impurities, and concentrating again to the usual consistency.

Purification of the starch before it enters the converter appears to be the only practical measure that can be taken to provide a syrup that is generally

satisfactory. Some improvement may be effected by the use of masking flavors, but the product is still inferior in taste and appearance to syrups prepared from 'hard' or 'prime quality' starch.

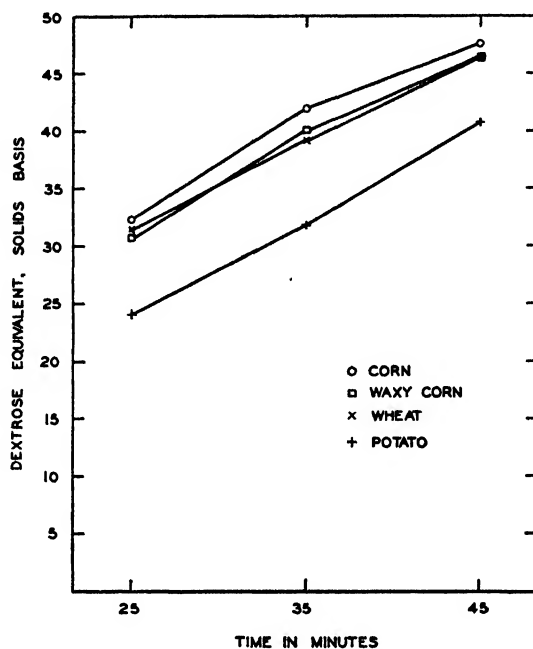


FIG. 2. Hydrolysis of 12° Bé. starch slurries with 0.2% hydrochloric acid (d.s. basis) at 35 p.s.i.

TABLE V

EFFECT OF PROTEIN CONTAMINATION ON THE HYDROLYSIS OF 23° BÉ. WHEAT STARCH SLURRIES WITH 0.2% HYDROCHLORIC ACID D.S. BASIS, AT 35 P.S.I.

The present data refer to wheat starch - 'vital' gluten mixtures

Conversion time, min.	Protein content of starch, %		
	0.4 (Control)	0.8	1.6
	Dextrose equivalent values of hydrolyzates		
25	44.5	41.6	45.1
35	57.3	59.5	56.8
45	64.8	71.6	61.4

Neutralization

In selecting a neutralization point for routine applications, a balance must be struck between filtration rate, filtrate clarity, and residual acidity. The adopted pH of 5.0 proved uniformly satisfactory on all starches; this indicates that the isoelectric point of the protein impurities is approximately at this acidity level. The filtration rate of wheat starch hydrolyzates drops off

sharply and the filtrates are turbid above a pH of 5.3. The filtrates are clear and filtration is rapid at pH values as low as 4.0. The protein dispersion that occurs on completely neutralizing cereal and potato starch hydrolyzates to pH 7.0 leads to serious frothing in the evaporator and also causes turbidity in the finished syrup.

Bartling (2) has prescribed the addition of 1½ gal. of 5% tannic acid solution to each 2000 gal. batch of corn starch hydrolyzate following neutralization and filtration. The effectiveness of this treatment in removing residual nitrogenous impurities was tested on crude hydrolyzates obtained from unrefined 16° Bé. wheat starch slurries. The above proportion of tannic acid solution was added to separate lots before and after the first filtration, with and without acetate buffering to pH 5.0. The nitrogen content of the finished syrup was not reduced by the addition of tannic acid to the unfiltered hydrolyzate, and was not affected by acetate buffering. Ten per cent reduction of the residual nitrogen content occurred with tannic acid additions following the first filtration. Higher tannic acid concentrations were not tested since the flavor of tannic acid was already evident in the product at the above level. Some improvement in taste quality may be obtained by the addition of tannic acid in the preparation of low quality syrups from impure starches, but this should be regarded as a direct result of its flavor rather than of its weak protein-precipitating action.

Protein and fatty impurities are the chief substances rendered insoluble by incomplete neutralization of cereal starch hydrolyzates, approximately 70% of the total nitrogenous impurities being removed at this stage. Potato starch contains less of these two classes of impurities, and losses of insoluble solids on the filter press are correspondingly smaller (Table VI). The data of

TABLE VI
LOSS OF INSOLUBLE SOLIDS ON FILTER PRESS (FROM 7 KGM. STARCH SOLIDS)

Source	Solids removed, gm.	% of total converted solids
Corn	86	1.23
Wheat	87	1.24
Potato	22.5	0.32

Table VI indicate that approximately 1% higher yield of syrup solids is obtained with root and tuber than with cereal starches. According to Bartling (2), the yield of corn syrup solids under industrial conditions varies from 101 to 104% of the dry starch weight.

Decolorization

The requisite amount of activated carbon can never be defined precisely because of the variations in requirements with differences in processing conditions and purity of raw materials. The amounts that have been prescribed

previously for complete decolorization range from 0.4% (8) to 4% or more (2) of the syrup solids.

The data of Fig. 3 illustrate the important differences in activated carbon (Darco S-51) requirements that were observed when tap water and distilled water were employed in the conversion. The hydrolyzates were prepared

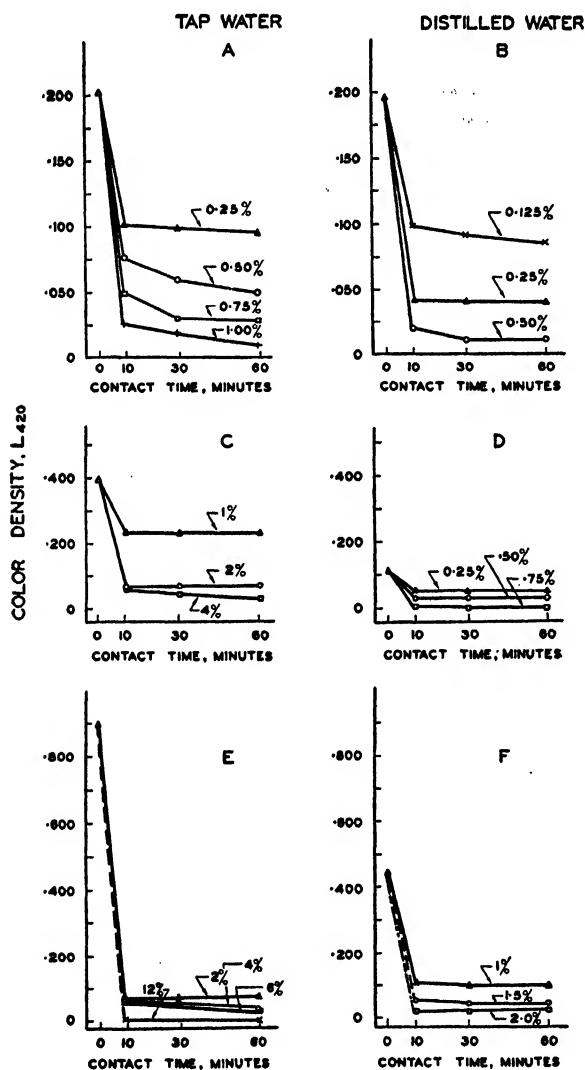


FIG. 3. Decolorization at 80° C. of wheat syrups prepared with distilled water and tap water. Carbon treatments are expressed as percentages of the liquid weight.

A and B, First decolorization at 14° Bé.

C and D, Second decolorization at 30° Bé.

E and F, Single decolorization at 30° Bé.

from wheat starch of high quality, which contained 0.35% protein. The amounts of carbon that were required in the first decolorization are shown in Fig. 3, A and B. Although the hydrolyzates were of similar color intensity, approximately twice as much carbon was required for equivalent decolorization at this stage in the presence of tap water. Considerably less color developed during evaporation to 30° Bé. when distilled water was used (Fig. 3, C, D). The quantity of carbon required at this stage (to 90% transmission at 4200) was reduced from 4% of the 30° Bé. syrup weight to 0.50% by the use of distilled water. Extending the contact time beyond 10 min. did not effect further color removal at this syrup density (Fig. 3, C, D). Four per cent and 1.5% carbon on the 30° Bé. syrup weight was required in the presence of tap water and distilled water, respectively, for equivalent decolorization by a single treatment at 30° Bé. (Fig. 3, E, F).

Employing distilled water, the over-all carbon requirements for colorless syrup production were 1.35% of the syrup solids with the conventional two-stage treatment, and 2.7% with a single decolorization at 30° Bé. The corresponding requirements in the presence of tap water were far greater (9.8 and 7.1%). The required quantity of activated carbon evidently is greatly increased by impurities introduced with the water used in slurry preparation. The importance of this effect cannot be adequately assessed from the present data, which are based entirely on local water. The results suggest, however, that a considerable reduction in the carbon requirement may be effected through the use of evaporator condensate or otherwise purified water.

The opinion expressed by Allen (1, p. 183) concerning the usefulness of bone char in starch syrup production is still widely held, i.e., "there has never been found a material that will exactly take the place of bone black in decolorizing and removing the bitterness from glucose (syrup) and corn sugar liquors".

In our experience, analytical data for syrups prepared with bone char and activated carbon have not indicated any marked superiority for the bone char syrups. No superiority was shown with respect to total ash (mainly sodium chloride), total nitrogen, or color development either on heating or during prolonged storage. Syrups possessing an off-flavor resulting from excessive protein contamination of the starch also were not noticeably improved by filtration over bone black. Bone char was found superior with respect to the adsorption of traces of dissolved copper and iron, as well as of the salts in industrial water that are responsible for storage haze in syrups prepared from starches of high quality. The very high efficiency of the revivification process largely accounts for the extensive use that continues to be made of bone char in starch syrup production. There may be other more elusive advantages gained through the use of char, but no clear-cut evidence of these was obtained in the present study.

Development of Color and Fluorescence in Stored Starch Syrups

A light amber color was developed during lengthy storage of syrups that were prepared from different types of starch and that had initially been decolorized with various brands of activated carbons or with bone char. Pronounced

storage color development was associated with a mild molasses-like flavor. Color formation could not be ascribed to a change in pH, and it was not influenced noticeably by the density or water content for the range 40° to 43° Bé., or by degree of conversion between 40 to 55 D.E. Color development also was not affected by extracting the hydrolyzate with ethyl ether; this indicates that the traces of hydroxy methyl furfural formed in the converter are of minor importance.

The syrups referred to in Table VII were prepared from tap water slurries of the commercial corn, wheat, and potato starches whose composition is shown in Table I, and of wheat starch to which gluten was added to provide

TABLE VII

EFFECT OF SULPHUR DIOXIDE ON COLOR DEVELOPMENT IN CORN, WHEAT, AND POTATO SYRUPS DURING TWO MONTHS' STORAGE AT ROOM TEMPERATURE

(All syrups initially colorless)

Source	Protein content, % d.s.	Color density, L420		
		SO ₂ content, p.p.m.		
		0	200	400
Corn	0.11	0.097	0.039	0.034
Wheat	0.13	0.119	0.101	0.039
Wheat	0.48	0.297	0.264	0.135
Potato	0.04	0.056	0.021	0.013

1.6% protein. All syrups had dextrose equivalent values of 50 ± 2 , were initially colorless, had a pH of 5, and a density of 42.0° Bé. at 100° F. Color development during two months' storage in diffuse light at room temperature was promoted by nitrogenous impurities and was inhibited by sulphur dioxide. Its stimulation by light is illustrated by Fig. 4. An increase in fluorescence

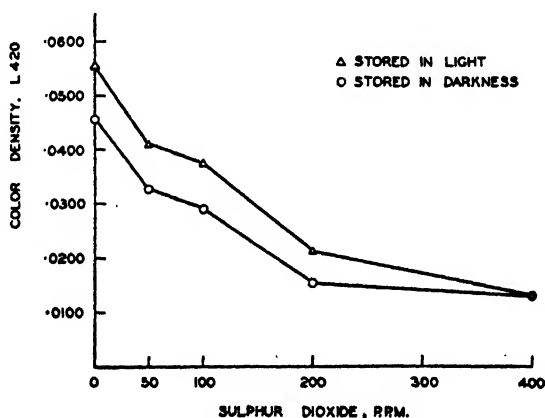


FIG. 4. Effects of light and sulphur dioxide on color development in 42° Bé. potato syrup during two months' storage at room temperature.

(Table VIII) was also observed during storage of wheat syrup, which showed general similarity to color development in that it was depressed by sulphur dioxide and was stimulated by a high content of nitrogenous impurities.

TABLE VIII

EFFECT OF NITROGENOUS IMPURITIES AND SULPHUR DIOXIDE
ON THE DEVELOPMENT OF FLUORESCENCE IN WHEAT SYRUPS
DURING TWO MONTHS' STORAGE

All measurements were taken on 20 gm. syrup diluted to 100 cc.

The fluorescence value for freshly prepared syrup was 8.0 units.

SO ₂ , p.p.m.	Nitrogen content, as % protein	Fluorescence value
0	0.13	16.0
	0.48	28.4
200	0.13	15.2
	0.48	27.5
400	0.13	14.0
	0.48	22.2

The foregoing data indicate that storage color development is a result of Maillard reactions between reducing sugars and nitrogenous compounds. When acid-extracted carbon and distilled water were used in preparing syrups from the starches of Table I, the products remained free of color for six months and were only delicately tinted after one year's storage in diffuse light at room temperature. Apart from the use of bisulphite and starch of low protein content, the most effective control measure apparently consists of excluding the catalytic impurities that can be introduced with the process water and carbon.

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SENSITIVITY OF CALCIUM SILICIDE SMOKE MIXTURES TO STATIC ELECTRICAL DISCHARGE¹

BY ARCHIBALD GILLIES²

Abstract

Sensitivity to ignition of the three component system, calcium silicide, hexachloroethane, and zinc oxide, was studied. Apparatus is described and results plotted as isopotential lines on a trilinear chart. The investigation disclosed that mixtures of widely varying composition may be easily ignited and are therefore highly dangerous. Technological application of the deductions is discussed.

Introduction

During the recent war a number of fires accompanied by fatalities occurred in both Canadian and American plants preparing calcium silicide smoke mixtures. After one serious accident in Canada and another in the United States these mixtures were prepared in fireproof rooms, the machinery and handling devices being manipulated by remote control by workmen in adjoining rooms. This lessened the probability of fatalities, but did not reduce the loss of costly and non-replaceable equipment, the output of which was sorely needed by the armed forces. All possible precautions were taken to protect the lives of workmen in the plants while investigations were conducted to determine, if possible, the underlying cause of the fires. Sabotage was entirely ruled out and the cause, if not the actual means of initiation, sought within the three component system itself.

This paper describes the investigation of one aspect of the problem having a fundamental bearing on the fires. While no suggestions are offered regarding the initial means of ignition, it makes clear the underlying conditions that make initiation possible and propagation much more rapid than was expected with such mixtures.

Materials

The materials used in this work were taken from shipments received at the filling plants. The present study was made on what is officially known as Smoke Mixture 264A. This consists of:

Calcium silicide	10%
Hexachloroethane	45%
Zinc oxide	45%

When thoroughly blended this mixture burns relatively slowly. This behavior led to the misconception in smoke filling plants that the mixture was rather

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inert and quite safe to handle. Such is true for the properly blended materials in the above mixture, but is not true for all possible combinations of the three components.

Methods of mixing used prior to this investigation had produced, during the process, compositions too close to the potentially dangerous ones, and the fires that took place are an indication that within the general mixture there were zones of highly sensitive composition. This, no doubt, had occurred many times but only rarely were all conditions right for ignition of the batch. There is no reason to believe that subsequent methods of mixing eliminated all danger, but it is known that in Canada, following adoption of recommendations arising out of this investigation, no fires took place in mixers preparing Smoke Mixture 264A during the remaining years of the war.

Apparatus and Experimental

After some preliminary tests on a wide range of mixtures of the three components it became clear that there was a great difference in the ease with which some mixtures ignited and in the rate at which they burned. Consequently, series of tests were made covering the range of mixtures that was of interest.

Use was made of a static electricity generator designed and constructed for the Explosives Laboratory by the Mechanical Engineering Division, N.R.C. (Fig. 1).

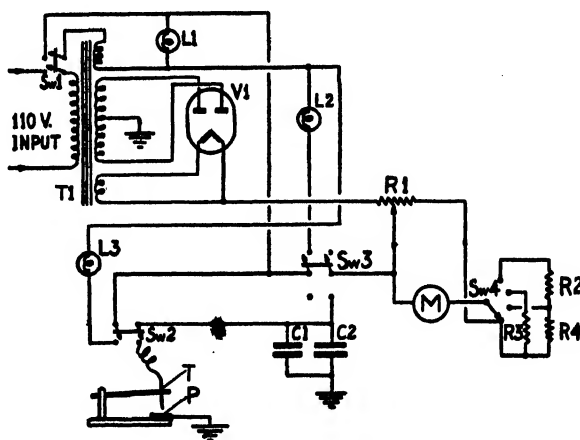


FIG. 1. Diagram of static electrical generator.

C1 and C2 combined, constitute a 14 mf. condenser that can be charged to the limit of 400 v. By proper manipulation of the resistances any desired voltage within the limits may be chosen. By means of switch Sw3 the charged condenser is isolated from the power source, and is discharged through the sample on the grounded plate, P, when the pointer, T, is lowered into the sample.

The sample was prepared from calcium silicide ground as finely as possible in an iron mortar. All three reactants were then ground together in an agate mortar. As all components were of high quality they received no other pre-

PARTS FOR STATIC GENERATOR

Item	Description
V1	Tube—Type 80
T1	Transformer, Hammond No. 272
M	Voltmeter, 0–50 v.
C1	Condenser, 4 mf. 600 v. oil filled
C2	“ 10 mf. “ “
R1	Potentiometer 25K
R2	Resistor, 50K
R3	“ 25K
R4	“ 6250 Ω
Sw1	Switch D.P.S.T.
Sw2	“ D.P.S.T.
Sw3	“ D.P.D.T.
Sw4	“ 4 position selector
L1	Lamp, 6 v. (blue)
L2	“ 6 v. (green)
L3	“ 6 v. (red)
T	Pointer to discharge condenser
P	Grounded sample plate

paratory treatment. Half-gram samples were placed upon the clean, grounded plate, *P*, and the condenser charged to a desirable potential. A little experience made it possible to know approximately what voltage to try. After the condenser was isolated from the power source the pointer, *T*, by means of its movable, insulating support, was lowered into the sample until it discharged. If a sample ignited, a lower voltage was used and other samples from the same mixture tried until a voltage was reached at which the sample would not ignite. Another sample was then examined usually at 5 v. above the previous potential. If this ignited, the potential was lowered again by 5 v. and another sample tested. If this failed to ignite, the previous voltage at which burning took place was taken as the minimum. The percentage of calcium silicide was held constant while the other two components were varied and the minimum potential for ignition of each mixture determined. From these data the minimum ignition potential of the most sensitive mixture for a fixed silicide content was chosen. The data for 50% silicide content (Table I) will illustrate the method.

TABLE I

MINIMUM POTENTIALS REQUIRED FOR IGNITION OF MIXTURES CONTAINING
50% CALCIUM SILICIDE

Weight per cent			Minimum potential
CaSi ₂	C ₂ Cl ₆	ZnO	Volts
50	5	45	35
50	10	40	31
50	15	35	30
50	20	30	30
50	25	25	35
50	30	20	45

When plotted, these data give a minimum value of 28 v. This value was then plotted against 50% calcium silicide in Fig. 2 and the same procedure repeated for other silicide values. Plotting all the minimum values against silicide content gives the graph in Fig. 2.

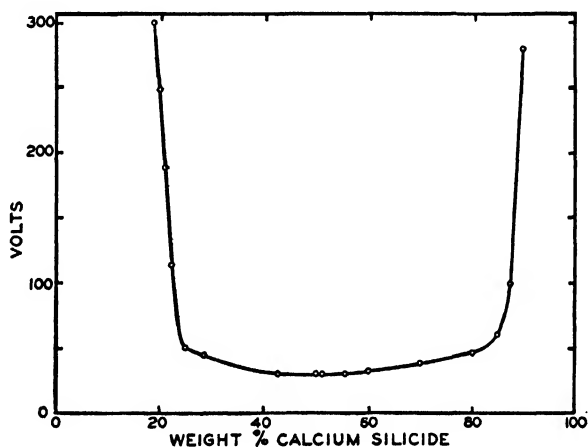


FIG. 2. Minimum ignition potential versus calcium silicide content of the system hexachloroethane, zinc oxide, and calcium silicide.

Results and Discussion

The information in Fig. 2 makes it quite clear that there is a wide range of mixtures with silicide content varying from about 20% to 90% that can be readily ignited. These mixtures are therefore highly dangerous if plant methods permit such compositions to occur in the process of mixing the six to seven hundred pound batches. All the information gathered from the aforementioned tests was used to plot isopotential lines on a trilinear chart (Fig. 3). An attempt was made to draw the curves in such a manner that they always represented the minimum potential required for ignition, i.e., the intervening areas may include some points having higher values but rarely any of a lower value. This gives at once a complete picture of the system so far as it was of

interest in the blending of smoke mixtures. An area of high sensitivity lies around the region marked *S*. By inspection of the isopotential lines this can be seen to be a wide region of varying compositions. The boundaries of this area are quite sharp, the potentials rising quickly with but small change in the composition of the mixtures. Thus, cross sections tend to resemble the curve shown in Fig. 2.

No values were determined for the area lying below the region marked *S* (Fig. 3). This was not needed for technological application, but would have been desirable as a matter of interest. However, the chart is very suggestive of the location of the uncompleted lines.

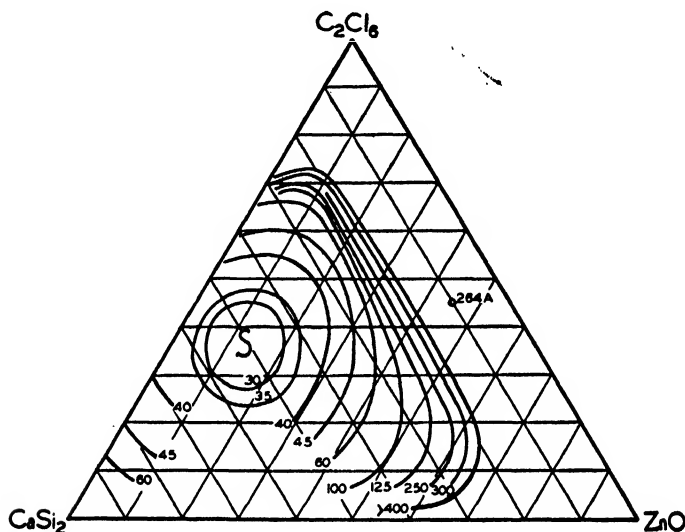


FIG. 3. Ignition potentials of the three component system hexachloroethane, zinc oxide and calcium silicide.

If mixtures lying within the area of low ignition potentials could be avoided, the probability that fires would start would be greatly reduced. This is possible by approaching the final composition (marked 264A on the chart) from the 50 : 50 zinc oxide – hexachloroethane mixture. This 50 : 50 mixture was well blended, and with continued mixing the calcium silicide was slowly added. This and slight modifications of this procedure were used to avoid, as much as possible, the highly dangerous compositions lying within the low potential area. The lack of subsequent fires in 264A mixers would suggest that some benefit had been gained from the study of this system.

Acknowledgment

The assistance of personnel of the Mechanical Engineering Division, N.R.C., who designed and built the static electricity generator, and of Macdonald Chemicals Ltd., Waterloo, P.Q., who supplied the chemicals, is gratefully acknowledged.

THE FP-54 AS A STABLE VOLTAGE AMPLIFIER¹

BY N. T. SEATON²

Abstract

A very simple method is given for operating the FP-54 Pliotron as a stabilized voltage amplifier with a grid current of less than 10^{-17} amp. The application of the method in the construction of a compact portable electrometer is discussed briefly.

General Discussion

The low grid-current characteristics of the FP-54 Pliotron make it an excellent electrometer tube. However, in most applications a difficulty is encountered in eliminating small voltage drifts in the associated circuit that result in instability. This difficulty is usually met by employing either heavy duty batteries and perhaps counter cells, or some form of bridge circuit. Considerable material has been written on the stabilization of the FP-54 as a current amplifier and a review of the various circuits employed has been given by Penick (5). Macdonald (3) has given an excellent discussion of d-c. amplifiers and the characteristics of the FP-54. Apparently little has been said however about the stabilization of this tube as a voltage amplifier, although it has been used as such by Müller and Shriver (4), Heidelberg and Rense (2), and others.

Inasmuch as the basic difficulty in stabilizing the FP-54 arises from the rapid change of space current with filament voltage, we will consider only stabilization against filament voltage variation. Stabilization against temperature variation in the other voltages can if necessary be obtained by the use of counter cells (7).

The basic circuit employed by the author is given in Fig. 1. For the plate voltage to be independent of the filament voltage we require $dE_p/dE_f = 0$ and thus that $dI_p/dE_f = 0$. Now consider operation at constant control-grid and plate voltage, then

$$\frac{dI_p}{dE_f} = \frac{\partial I_p}{\partial E_f} + \frac{\partial I_p}{\partial E_s} \cdot \frac{dE_s}{dE_f}, \quad (1)$$

and further

$$\frac{dE_s}{dE_f} = -R_t \cdot \frac{dI_s}{dE_f} = -R_t \left(\frac{\partial I_s}{\partial E_f} + \frac{\partial I_s}{\partial E_s} \cdot \frac{dE_s}{dE_f} \right). \quad (2)$$

Solving Equation (2) for dE_s/dE_f , and defining $\partial I_s/\partial E_s = 1/R_s$, we obtain

$$\frac{dE_s}{dE_f} = \frac{-R_t}{1 + R_t/R_s} \cdot \frac{\partial I_s}{\partial E_f}. \quad (3)$$

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Further defining $\partial I_p / \partial E_s = g_m$, and applying the condition $dI_p / dE_f = 0$, we obtain from Equations (1) and (3) the stabilization condition

$$\left(\frac{\partial I_s}{\partial E_f} / \frac{\partial I_p}{\partial E_f} \right) \cdot \frac{g_m \cdot R_l}{1 + R_l / R_s} = 1. \quad (4)$$

The above condition, Equation (4), may be met for almost any values of filament and grid voltage; however, a filament voltage of about 1.2 v. would seem most desirable. The low emission of a microampere or so accompanying this filament voltage minimizes the grid current without reducing the plate current to too small a value. For most purposes all voltages can be obtained from ordinary radio dry cells.

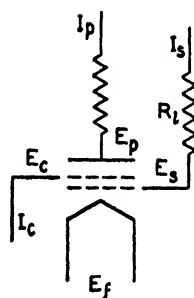


FIG. 1. Basic circuit of the FP-54 voltage amplifier. For an appropriate choice of the operating conditions and of the space charge grid load resistor, R_l , the plate current becomes stabilized against filament voltage variation.

Operation Conditions

The large variation in the characteristics of different FP-54's has been noted by various workers; Fig. 2 is an example of this from the present work. In some cases it has been possible to greatly simplify representation of the data (which can only be approximate in view of the above variation) by making certain assumptions.

It is evident* from the characteristics of Fig. 2 that the space current, I_s , is essentially saturated for $E_s > 2$ v.; although the issue is somewhat clouded in the case of Tube 2. Indeed, if we consider the distribution of voltage along the filament, we see that saturation begins to take place for an E_s of about 0.7 v. The first knee of the curves then corresponds to the 'end-effect' (due mainly to a temperature decrease) around the midpoint of the filament (inverted-V type), and should occur for an E_s of about $\frac{1}{2}(1.2 \text{ v.}) + 0.7 \text{ v.} = 1.3 \text{ v.}$, while the second knee corresponds to saturation being attained along the entire length of the filament and should therefore occur at $1.2 \text{ v.} + 0.7 \text{ v.} = 1.9 \text{ v.}$

* See, for instance, F. E. Terman, "Radio Engineering," 1937, Figs. 50a and 51.

If we neglect the effect of small changes in E_f , per se, upon the distribution of I_{s0} to the plate and space charge grid, and assume saturation, then it follows that we may replace $\frac{\partial I_s}{\partial E_f} / \frac{\partial I_p}{\partial E_f}$ by I_s/I_p and obtain as a useful approximation to Equation (4)

$$(I_s \cdot g_m / I_p) \cdot \frac{R_l}{1 + R_l/R_s} = 1. \quad (5)$$

An additional consequence of this assumption is that the space current, $I_s + I_p = I_{s0}$, should be independent of the plate current, I_p , and consequently of the control-grid and plate voltages, E_c and E_p respectively. This approximation is valid over a very wide range of operating conditions.

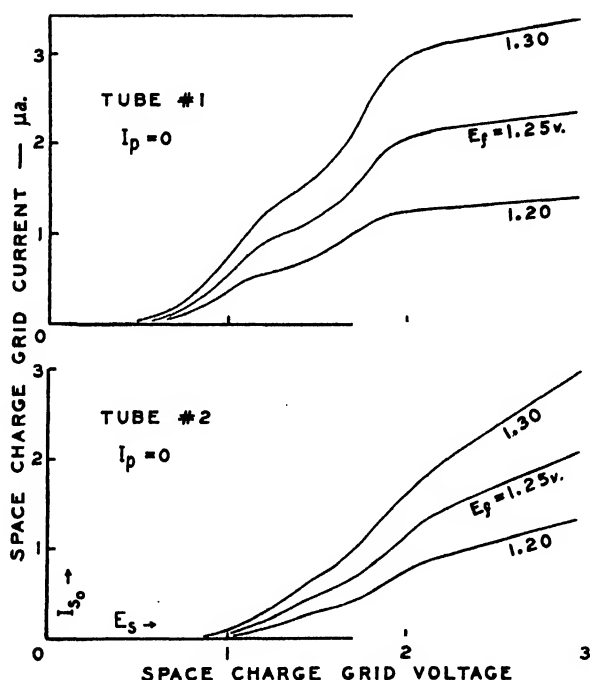


FIG. 2. Space current characteristics of the FP-54, showing the variation that may exist between individual tubes. The space current, $I_s + I_p$, is essentially independent of I_p and hence can be represented by I_{s0} .

It is further of interest that the transconductance, g_m , may be regarded, first, as independent of the space charge grid voltage, E_s , for $1.6 \text{ v.} < E_s < 2.4 \text{ v.}$, and second, as a function of I_p/I_s rather than of E_c and E_p .

In an actual circuit the presence of the space charge grid load resistor, R_l , effectively decreases the plate resistance, R_p , slightly for all I_s/I_p less than about 30, but leaves the amplification factor unchanged. These dynamic values are given in Table I. The effect may be shown mathematically if we take $(\partial I_{s0}/\partial E_c)/I_{s0} = (\partial I_{s0}/\partial E_p)/I_{s0} = 0.04 \text{ } \mu\text{mho}/\mu\text{a. emission}$.

TABLE I

TYPICAL CONDITIONS FOR OPERATING THE FP-54 AS A STABLE VOLTAGE AMPLIFIER

(The E 's are actual electrode voltages, not supply voltages.)

	Condition 1	Condition 2		Condition 1	Condition 2
E_f	1.2 v.	1.2 v.	I_p	0.1 μ a.	0.1 μ a.
I_f	65 ma.	65 ma.	R_t	1 meg.	1 meg.
E_s	2.0 v.	2.0 v.	R_p^*	7 megs	10 megs
E_c	-1.5 v.	-4.5 v.	μ^*	0.6	1
E_p	3.0 v.	5.5 v.	I_c	$< 5 \times 10^{-17}$ amp.	$< 1 \times 10^{-17}$ amp.
I_s	1.0 μ a.	1.0 μ a.			

* Dynamic values.

TABLE II

CONDITIONS AT A POINT OF FIRST ORDER STABILITY FOR WHICH THE SPACE CHARGE GRID VOLTAGE IS BEYOND THE SECOND KNEE OF THE SPACE CURRENT CURVE (FIG. 2). AN INCREASE OF FILAMENT AND PLATE CURRENT WILL LEAD TO A POINT OF SECOND ORDER STABILITY. SEE ALSO FIG 5.

E_f	E_s	I_s	I_p	g_m	R_t	R_s
1.17 v.	2.2 v.	0.8 μ a.	0.05 μ a.	0.07 μ mho	1 meg	6 megs

Satisfactory stabilization can be had for any reasonable grid bias, and representative conditions are given in Table I. Control characteristics are given in Fig. 3. The value of the grid current for condition 1 of Table I was

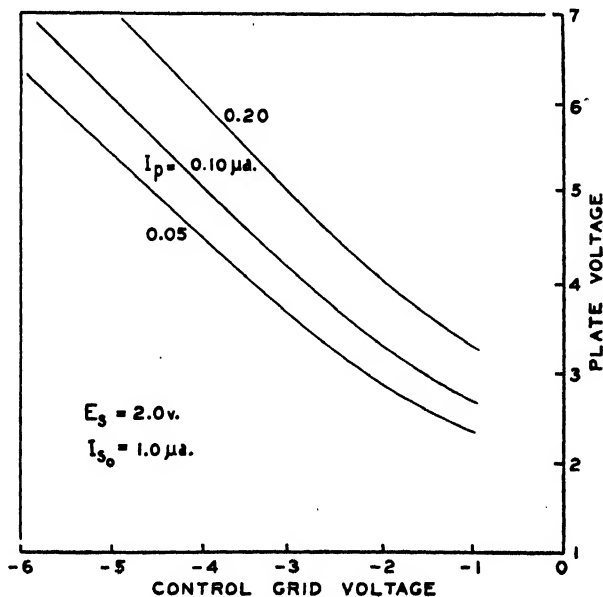


FIG. 3. Control characteristics of the FP-54. These do not vary widely for different tubes.

consistently obtained for both new tubes used by the author, and is considerably lower than expected on the basis of Macdonald's (3) results.

Stabilization

The most rapid method of obtaining stabilization is by experiment, and the following analysis should act as a guide. We consider the case where I_s/I_p is of the order 10. We may then regard R_s as independent of I_p (and hence E_p) and obtain it from Fig. 2. To attain the first order stabilization condition of Equation (5), it is best to choose first an approximately suitable value of R_s , and then to vary E_p , which controls only the first factor. The effect of E_p on the first factor of Equation (5) is shown in Fig. 4. The single control used to vary E_p , say a variable plate load resistor, further permits adjustment to a condition of second order stability.

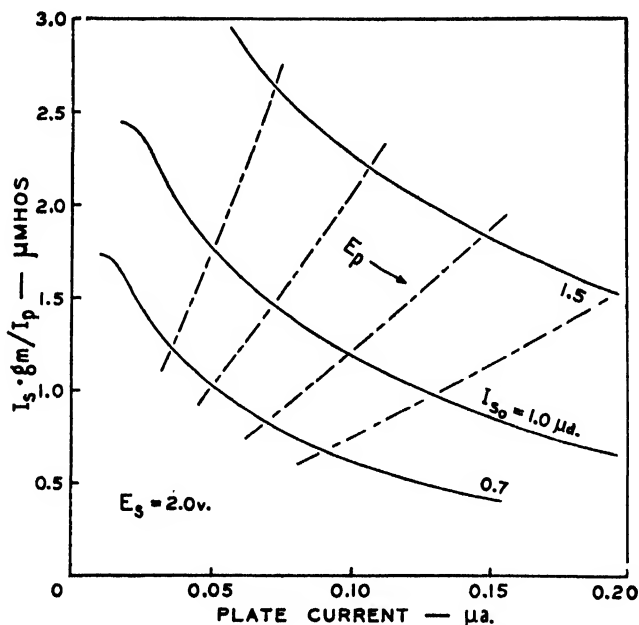


FIG. 4. Plot of the first terms of the balance Equation (5). The dashed lines represent equal increments in E_p (or decrements in E_s) of about 0.3 v.; the actual value of E_p for a given I_p depends of course on E_s . (See Fig. 3.) The different values of I_{s0} are obtained by varying E_s . (See Fig. 2.) These characteristics vary considerably for different tubes.

For second order equilibrium we require not only that Equation (4) be satisfied, but also that its derivative with respect to E_s be zero. For our considerations the latter condition may be put in the convenient form

$$\frac{\partial}{\partial I_{s0}} (I_s \cdot g_m / I_p) = \frac{\partial}{\partial I_{s0}} (1/R_s) + \frac{1}{2} (I_s \cdot g_m / I_p)^{-1} \frac{\partial}{\partial E_s} (-1/R_s). \quad (6)$$

The left side of Equation (6) can be obtained from Fig. 4 while both positive terms on the right can be obtained from Fig. 2. It is then seen that second order stability occurs for E_s in the region of the second 'knee' (Fig. 2), i.e., for $E_s \cong 2$ v.

Suppose for example we consider a specific tube, for which the stability curves of Fig. 5 apply. The conditions at the maximum of Curve A are given in Table II; these evidently satisfy Equation (5), the condition of first order

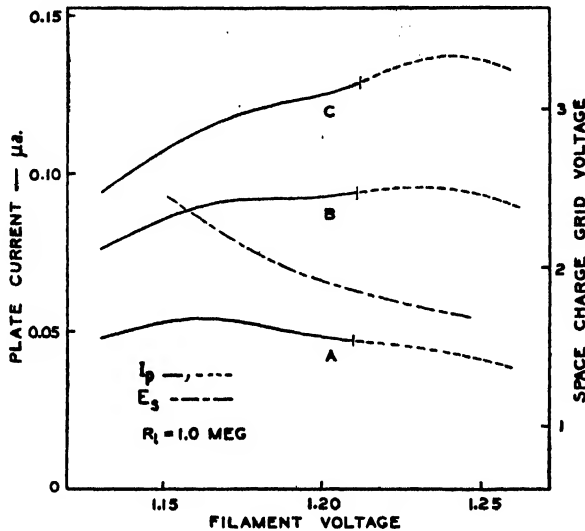


FIG. 5. Typical stability curves showing that second order equilibrium is obtained by the appropriate adjustment of the plate current I_p . In general the sections (dotted above) corresponding to operation below the second knee of the I_p vs. E_s curves (Fig. 2) vary widely with different tubes, and although points of second order stability are often observed in this region, their determining factors would seem neither readily nor consistently found.

stability. As I_p is increased, the maximum occurs at increased filament voltage, until finally the emission is such that $E_s \cong 2$ v. and the maximum becomes a point of inflexion, as in Curve B, giving second order equilibrium. Curve C shows the result of a still further increase in I_p . With second order stability it should be possible to vary E_s by 2% or so without changing I_p more than 0.1%. In an actual voltage amplifier circuit, the corresponding change in E_p is limited by the plate resistance, R_p , to about 1 mv. for the conditions of Table I.

The above discussion has been based on the use of E_p as a variable for obtaining stability. Although a variable R_l , with a fixed E_p , may be used to obtain first order stability, it cannot in general be used to obtain second order. However, if the tube is operated with essentially constant I_p (i.e., a large plate load resistor is used), a series of curves similar to those of Fig. 5 in the order A, B, C, can be obtained by increasing R_l (and decreasing E_f to keep $E_s \cong 2$ v.).

PLATE I

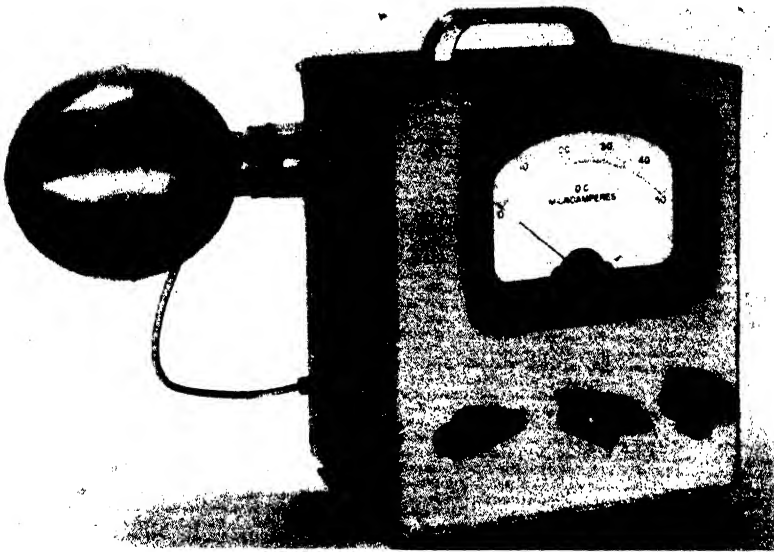


FIG. 6. A portable electrometer using the stabilized FP-54 circuit. A 10 cm. diameter spherical ionization chamber is attached to the input. At the upper left are the lever switch and the switch S of Fig. 7, while the controls below the meter are: the filament control, the range switch, and the fine zero-setting control. The coarse zero-setting control is adjustable from beneath the base.

amplification. The accompanying decrease in the resistive component of the input impedance greatly reduces the time constant of direct-reading instruments. Further examples of negative feed-back amplifiers have been given by Vance (8), Roberts (6), Heidelberg and Rense (2) and Harnwell and Ridenour (1).

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ROT RESISTANCE OF COTTON DUCK TREATED WITH CHELATE COPPER COMPOUNDS¹

BY W. I. ILLMAN², G. SEMENIUK³, A. C. NEISH⁴, AND G. A. LEDINGHAM²

Abstract

Thirteen organic compounds capable of forming chelate complexes were used to fix copper in cotton duck. Their rotproofing effectiveness was then determined by the loss in tensile strength during soil burial. The compounds tested were, in order of decreasing effectiveness, cupferron, 8-hydroxyquinoline, 1-nitroso-2-naphthol, dimethylglyoxime, salicylaldoxime, glucose oxime, diphenylthiocarbazone, rhodanine, benzoin oxime, *s*-diphenylcarbazide, acetoin oxime, and fructose oxime. Copper complexes formed with cupferron and 8-hydroxyquinoline possessed rot resistant properties far superior to those of copper naphthenate or any of the other compounds tested.

Introduction

Since the discovery of the Bordeaux Mixture, the application of copper compounds to various problems of fungal control has been most extensive. For the purpose of rotproofing textiles, compounds that have received most attention are copper salts of organic acids, particularly the copper naphthenates.

Organic reagents that form chelate complexes with heavy metals have received very little attention as fixatives for copper in textiles. Zentmyer (6) showed that 8-hydroxyquinoline is an active fungistatic compound. Hatfield *et al.* (3, p. 38) used it to fix copper and other metals in textiles and found that this gave them resistance to rotting. Dimethylglyoxime has also been shown in these laboratories (4) to fix copper in fabrics, thereby conferring a degree of rot resistance superior to that of the widely used reference compound, copper naphthenate.

The purpose of the present work was to compare the rotproofing effectiveness of a number of cupric complexes of organic compounds capable of forming covalent linkages with metals. The compounds used were 8-hydroxyquinoline, dimethylglyoxime, salicylaldoxime, benzoin oxime, acetoin oxime, fructose oxime, glucose oxime, 1-nitroso-2-naphthol, ammonium nitrosophenylhydroxylamine (cupferron), rhodanine, diphenylthiocarbazone, and *s*-diphenyl-

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carbazine. Since the utilization of Canadian peat residues was under study at the time, the copper compound formed from ammonium humate* was included.

A preliminary soil burial test showed that cupferron, 8-hydroxyquinoline, 1-nitroso-2-naphthol and dimethylglyoxime were the most promising; therefore, these were compared with each other and with copper naphthenate over a wider range of copper concentrations.

Experimental and Results

MATERIALS

Glucose, fructose, and acetoin oximes were prepared by treating the carbonyl compounds with hydroxylamine in alcoholic solution at room temperature for 30 days. They were not isolated but the solutions obtained were diluted and used directly. A commercial grade copper naphthenate containing 10% copper was used in Stoddard solvent. The other organic compounds were obtained from Eastman Kodak Co. No. 8 unbleached cotton duck (18.5 oz. per sq. yd.) was chosen as a suitable fabric for impregnation.

PRELIMINARY COMPARISON OF DIFFERENT TREATMENTS

In the preliminary test it was assumed that varying the amount of organic compound put into the fabric would cause a variation in the amount of copper fixed. Accordingly, strips of cotton duck 6 by 11½ in. were treated in pairs with varying amounts of the organic reagents, mostly in ethanolic solutions. It was found necessary to add 1% of ethanolamine to the alcohol to dissolve diphenylthiocarbazone. Ammonium humates were applied to the fabric from boiling aqueous baths in serial dilutions from 3.0 to 0.09%. Subsequent to treatment, the strips of duck were dried in a horizontal position over a bed of nails held in position by a pressed wood fiber base. The horizontal drying, with frequent turning, was designed to give even impregnation with minimum draining.

Copper was fixed in the dried treated fabrics by immersion in an aqueous 2.5% cupric acetate solution. After two hours the fabrics were air-dried, then leached for two hours in running water. The glucose oxime complex was somewhat soluble, hence it was leached for only one hour.

The treated fabrics were cut into strips 6 by 2½ in. For each treatment, eight of these strips were buried at random; this allowed two lots of 40 breaking strength samples of 1 in. width for each compound. The soil used was a composted sandy loam moistened to 70% of its water holding capacity. It was in deep flats in a room maintained at 95 to 98% relative humidity at a temperature of 86° F.

Samples were dug up after 21 and 56 days' burial, washed free of soil, conditioned at $65 \pm 2\%$ relative humidity and 70° F. before breaking tests

* Kindly supplied by Mr. C. W. Davis, Division of Chemistry, National Research Laboratories, Ottawa, Canada.

were made. The wet breaking strength of the strips, each ravelled to 1 in. width, was determined on a Scott tester—with clamp jaws set 3 in. apart.

The results of the soil burial tests are shown in Table I. Although the organic reagents had been applied in one, two, three, four, and five millimole quantities, for each 6 by 11½ in. strip, the range of copper concentrations was narrower than that expected; this made it difficult to compare treatments on the basis of equal amounts of copper fixed. However, there were wide differences in the rotproofing capacity of the different compounds; thus it was possible to select a few superior ones for further work. Thus dimethylglyoxime, 8-hydroxyquinoline, 1-nitroso-2-naphthol, and cupferron were chosen and compared with copper naphthenate in the experiment described below.

TABLE I

LOSS IN TENSILE STRENGTH OF BURIED COTTON DUCK TREATED WITH COPPER-ORGANIC COMPOUNDS

Organic compound used to fix copper	Copper content, % of dry weight	Original breaking strength*, lb./in.	Breaking strength as % of original*	
			After 21 days' burial	After 56 days' burial
None	Nil	230	Nil	Nil
Fructose oxime	1.61 - 1.79	214	27	Nil
Acetoin oxime	1.40 - 1.49	201	60	2
s-Diphenylcarbazide	0.66 - 0.80	233	28	1
α-Benzoin oxime	0.91 - 1.12	186	58	15
Rhodanine	0.90 - 1.10	216	86	28
Diphenylthiocarbazone	0.45 - 0.55	174	94	18
Glucose oxime	0.68 - 0.73	198	94	21
Humates	0.58 - 0.75	208	113	28
Dimethylglyoxime	0.18 - 0.24	237	98	48
Salicylaldoxime	0.48 - 0.54	185	124	61
8-Hydroxyquinoline	0.79 - 0.91	213	91	80
1-Nitroso-2-naphthol	0.47 - 0.65	216	111	98
Cupferron	0.50 - 0.69	185	130	121

* Based on an average of 24 to 40 individual breaking strength determinations. A breaking strength of 'nil' means the duck was rolled so badly no complete strips could be found.

It should be noted from Table I that certain treatments lowered the original breaking strength of the strips. After burial in the soil for three weeks, those strips not readily attacked by molds actually showed an increase in strength up to the level of the original untreated material. These differences may be due to the initial presence of abrasive crystals in the treated fabric and to their subsequent removal during soil burial.

COMPARISON OF THE MOST PROMISING TREATMENTS

Impregnation of Fabrics

The method of impregnation in the first experiment made it difficult to control the amount of copper fixed, and, in some instances, affected the initial

breaking strengths. Therefore, further studies were made in this respect on each of the selected compounds. It was found that the amount of copper fixed was best controlled by varying the concentration of the copper bath rather than the amount of organic compound. Since these details are important, the exact procedure for each treatment is as follows.

Copper naphthenate.—A commercial grade copper naphthenate containing 10% copper was applied from solution in Stoddard solvent (1). Concentrations of 5, 10, 17, and 20% naphthenate in the solvent were found to provide for uptake on the fabric of 0.22, 0.57, 0.96 and 1.1% copper.

Copper dimethylglyoxime.—Dimethylglyoxime was applied to the duck from a saturated solution in water at 92° to 94° C. The individual strips of duck were thoroughly wetted out as they were introduced to the solution, allowed to remain in the treating bath for 20 min., rolled between blotters and air-dried. Copper fixation was obtained by immersing the duck in aqueous solutions at 1.1, 2.5, 3.5, and 6.0% cupric acetate. The amounts of copper fixed were found to be 0.4, 0.6, 0.85 and 1.2% of the dry weight following water leaching. Lower copper bath concentrations were found to be impractical for the fixation of a lower percentage copper on the fabric. A nonsaturated hot aqueous bath of dimethylglyoxime supplied an even impregnation of the oxime on the duck, which, fixed by a 1.1% copper acetate solution, supplied a final 0.2% copper. The copper treated fabric was dried by rolling between blotters and by exposure to air. In the tests with dimethylglyoxime it was found that hydrogen ion concentration in the copper bath, and the relation between concentration of the organic compound on the duck and the concentration of copper in the aqueous cupric acetate bath, are important factors governing this fixation.

Copper cupferron.—The cotton duck to be treated was immersed in an aqueous bath at room temperature containing 200 millimoles cupferron per liter and 0.01% Gardinol wetting agent. It was then partially air-dried in a horizontal position and immersed in cupric acetate baths of 0.5, 2.0, 3.5, and 6.0% to give concentrations in the fabric of 0.23, 0.60, 0.92, and 1.1% copper. The 6.0% copper bath contained just the excess of ammonia necessary to redissolve the copper. It contributed much more color to the fabric than the baths of low copper percentage containing no ammonia.

Copper 8-hydroxyquinoline.—A two-bath method recommended by the Monsanto Chemical Company (3, p. 38) was used. Thus the 8-hydroxyquinoline was converted to the acetate by boiling in glacial acetic acid and the resulting solution diluted with water to the desired concentration. The fabric was wet out with 0.01% Gardinol, rinsed several times in water, and finally treated by exposure to the solution of the organic compound at 94° C. for 20 min. Copper was fixed in the treated fabric only in acid solutions (pH 5.5 *ca.*) of cupric acetate. The concentrations of the treating baths are given in Table II, together with the resulting concentrations of copper on the fabric.

Copper 1-nitroso-2-naphthol.—The satisfactory impregnation of 1-nitroso-2-naphthol copper complex over a range of copper uptake values proved very difficult. Upon repeated occasions, it was found that the amount of copper

TABLE II

COPPER CONCENTRATIONS ON FABRIC FOLLOWING TREATMENT WITH 8-HYDROXYQUINOLINE AND COPPER ACETATE SOLUTIONS

Treating baths		Copper on fabric, % dry wt.
8-hydroxyquinoline, %	Copper acetate, %	
1.0	0.5	0.22
3.0	0.25	0.38
3.0	0.60	0.52
3.0	2.0	0.76
3.0	6.0	0.87
5.0	4.0	0.90

fixed following treatment with a saturated solution of 1-nitroso-2-naphthol in 95% ethanol was less than that fixed in copper baths of identical concentration following treatment with just one-half as much of the organic compound. For the burial test, a range of treatments was used in which from $\frac{1}{4}$ to 5 millimoles of the organic compound was applied to each 6 by 11 $\frac{1}{4}$ in. piece of fabric. The uptake following treatments is shown in Table III.

TABLE III

COPPER CONCENTRATIONS ON FABRIC FOLLOWING TREATMENT WITH 1-NITROSO-2-NAPHTHOL AND COPPER ACETATE SOLUTIONS

Treating bath		Copper on fabric, % dry wt.
1-nitroso-2-naphthol, %	Copper acetate, %	
1.3 in benzene	1.0	0.17
2.6 in ethanol	4.0	0.35
0.16 in ethanol	2.5	0.65
0.43 in ethanol	2.5	0.70
2.6 in benzene	6.0	1.0

Soil Burial Test

The conditions of soil burial were similar to those described for the first experiment. For each concentration of the five different treatments, eight fabric samples, 6 by 2 $\frac{1}{2}$ in., were buried at random in a vertical position with the upper end just exposed to view. In this way it was possible to obtain visible evidence of rotting without disturbing the samples. Four samples of each treatment were dug up after 35 days and the remainder after 90 days' burial. The breaking strengths were then determined as described above.

The results of the soil burial experiment are illustrated in Plate I and the tensile strengths presented in Table IV. Copper naphthenate was the least

effective of the compounds tested, all samples being completely disintegrated after 90 days' burial. Even after 35 days, at the highest copper concentrations

TABLE IV

EFFECTIVENESS OF MOST PROMISING TREATMENTS IN PRESERVING TENSILE STRENGTH OF BURIED COTTON DUCK*

Treatment	Copper content, % of dry weight	Original breaking strength, lb./in.†	Breaking strength as % of original‡	
			After 30 days' burial	After 90 days' burial
None	Nil	230	Nil	Nil
Copper naphthenate	0.22	225	Nil	Nil
	0.57	215	1	Nil
	0.96	226	14	Nil
	1.1	255	37	Nil
Copper dimethylglyoxime	0.20	218	6	Nil
	0.40	208	57	Nil
	0.60	211	65	Nil
	1.2	185	68	14
Copper 1-nitroso-2-naphthol	0.17	232	Nil	Nil
	0.35	242	2	1
	0.65	226	14	2
	0.70	243	91	59
Copper 8-hydroxyquinoline	1.0	239	—	91
	0.22	234	76	62
	0.38	190	97	74
	0.52	205	89	80
Copper cupferron	0.76	207	98	99
	0.87	234	85	93
	0.90	202	113	99
	0.23	233	96	73
	0.60	235	98	99
	0.92	218	107	107
	1.1	210	115	108

* No. 8 cotton duck buried in biologically active soil.

† Standard deviation of means was ± 15 lb.; each figure is average of eight breaks.

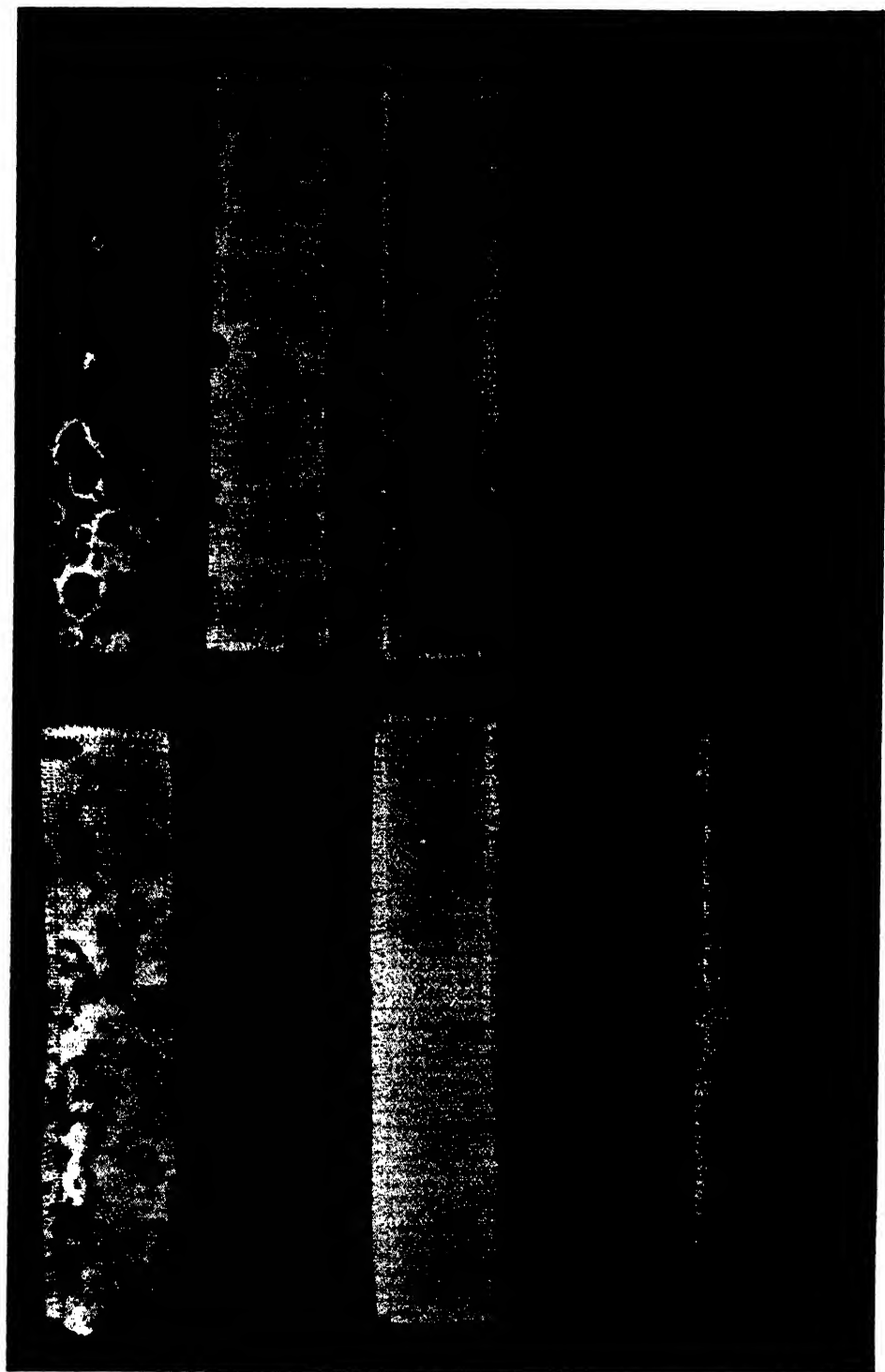
‡ A breaking strength of 'nil' means that the duck was rotted so badly no complete strips could be found.

EXPLANATION OF PLATE I

Strips of copper organic treated duck after soil burial for 35 days:

Label	Treatment	Copper content, %
A ₁	Copper dimethylglyoxime	0.20
A	"	0.60
B ₁ *	Copper naphthenate	0.22
B	"	0.57
C ₁	Copper-cupferron	0.23
C	"	0.60
D ₁ *	Copper 1-nitroso-2-naphthol	0.17
D	"	0.70
E ₁	Copper quinolinate	0.22
E	"	0.76

* Samples B₁ and D₁ were too far disintegrated to photograph.



the tensile strength was decreased to one-third of the original. The strip containing the lowest concentration of copper had disintegrated. Copper dimethylglyoxime was superior to both copper naphthenate and copper 1-nitroso-2-naphthol at the low copper concentrations, but inferior to the latter at high concentrations. As shown in Plate I, mold attacked it in localized areas, causing marked spotting of the fabric.

The 8-hydroxyquinoline and cupferron treatments were markedly superior to the others, there being no significant decrease in tensile strength even after 90 days' burial, if the copper concentration was 0.60 to 0.70% or higher. Cupferron may be slightly better at the lower copper concentrations. Except for slight spotting on these at the lowest copper concentration, there was no visible attack by molds.

Discussion

Of the two compounds most effective in providing rot resistance when fixed in cotton duck as chelate copper complexes, we prefer cupferron because it can be applied from aqueous solution at room temperature and because the treatment does not impart much color to the fabric. The color conferred was pale blue green to light bluish grey, while the color of the copper quinolate treated strips was strong yellow.

These studies arose from wartime 'tropicalization' work, and have now been discontinued. Since their termination, the weathering characteristics of cotton tenting treated with copper cupferron have been investigated by others (5) and compared with those of fabric treated by the standard cuprammonium process. Similar weathering data have been published for cotton duck containing the copper compounds formed by 8-hydroxyquinoline and by dimethylglyoxime (2).

It is hoped that investigators whose primary interests include fungicides will explore the potentialities of cupferron and other chemicals that form chelate copper complexes.

Acknowledgments

Thanks are due to Mr. C. H. Bayley for making available the facilities of the textile section of the Division of Chemistry, and to Mrs. M. W. Weatherburn, formerly of that section, for valuable criticism during the course of the work and for assistance in preparation of the manuscript. The technical assistance of Miss M. T. Clement, Mr. V. K. Wallen, and Mr. D. H. Grills is also gratefully acknowledged.

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THE RAPID DETERMINATION OF LOW CONCENTRATIONS OF CARBON MONOXIDE IN AIR¹

BY MORRIS KATZ² AND JOHN KATZMAN³

Abstract

A granular form of silver permanganate on a zinc oxide carrier has been found to oxidize carbon monoxide in air at ordinary temperatures and at high space velocities. There is no noticeable change in activity over the range of 30 to 100% relative humidity of the air, although a small amount of water vapor is essential to initiate the combustion of carbon monoxide. The above properties have been utilized in the rapid determination of low concentrations by measuring the heat of oxidation in a thermocouple cell. The relation between the potential of the thermocouple junctions and the concentration of carbon monoxide is linear over the range of 0 to 600 p.p.m. at a definite space velocity. With increasing flow rate at a constant concentration the potential rises rapidly to a maximum, but in the range of optimum flow the flow rate may be varied considerably without producing a major change in e.m.f. The thermal efficiency is about 81% at the optimum flow rate. Hydrogen, unless it is present in amounts considerably in excess of the carbon monoxide concentration, does not introduce an appreciable error in the determination. The method is applicable to the field determination of considerably less than 0.005% carbon monoxide in air and the degree of precision is about equal to that of most laboratory methods. Twenty to twenty-five cubic centimeters of the material will give a useful life of over eight hours in continuous tests on concentrations below 0.1% carbon monoxide.

Introduction

The detection and quantitative estimation of low concentrations of carbon monoxide in air is a matter of prime importance in safeguarding the health of personnel in industrial plants, mines, vehicles, and aircraft where this gas may occur in physiologically significant concentrations. At ordinary altitudes exposure to 0.01% for several hours may be tolerated without any noticeable effects, but at high altitudes, especially above 10,000 ft., as little as 0.005% may impair the efficiency of a pilot in an aircraft, with disastrous results. Any method of determining carbon monoxide should be accurate to 0.001% or less if it is to be applicable to all environmental conditions.

The subject of the toxicity of carbon monoxide, and the older methods of estimating this gas in air, have been reviewed at length by Drinker (1) and briefly by Katz (4). With the exception of more or less involved laboratory methods, such as the use of iodine pentoxide (3) and red mercuric oxide (8) at elevated temperatures, absorption of the carbon monoxide in blood by the Roughton and Van Slyke procedures (9), or oxidation of the carbon monoxide in a dried and carbon-dioxide-free sample over hopcalite at 100° C. and subsequent absorption of the carbon dioxide and acidimetric estimation (9)

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there was, until recently, no rapid method sufficiently accurate for the determination of carbon monoxide below 0.005%. The need for a rapid method of detecting concentrations in this range, particularly for aircraft, during World War II led to the development by the National Bureau of Standards of the United States (10) of a colorimetric indicator consisting of silica gel impregnated with palladium sulphate and ammonium molybdate. In field use a fairly close estimation of the concentration may be made by measuring the time at constant flow rate required to attain the color of a set of standard gel tubes. Accurate determinations may be made by a more complex laboratory method involving the use of fresh indicating tubes exposed to known concentrations of gas.

The material used in the present method was developed after a study by Katz and Halpern of the reaction between carbon monoxide and silver permanganate deposited on various metallic oxide carriers in an active granular form (5), such as a mixture of 69 mole % silver permanganate and 31 mole % zinc oxide. Although crystalline silver permanganate in the dry state exhibits virtually no activity in the oxidation of carbon monoxide at ordinary temperatures, and only moderate activity when the moisture content of the crystals is held between about 5 to 10%, the rate of oxidation may be increased enormously by deposition on a suitable metallic oxide carrier. Such preparations are then most active when the granules are thoroughly dry. The oxidation of carbon monoxide is quantitative and the concentration may be measured accurately by passage of the gas sample at a measured flow rate over these granules at room temperature. The material is nonhygroscopic and, unlike hopcalite, does not have to be protected by drying agents.

Hopcalite is a catalyst that has been used since World War I for the oxidation of carbon monoxide in air, either in gas mask canisters or in direct indicating instruments. It is a specially prepared granular mixture of manganese dioxide and cupric oxide (2). Owing to its susceptibility to poisoning by water vapor, this catalyst may be used only on dried gases, especially at ordinary temperatures. The silver permanganate - metallic oxide product, on the other hand, requires a small amount of water vapor to initiate the oxidation of carbon monoxide and in this respect its behavior is similar to that of palladium chloride. However, the water vapor normally present in air under all ordinary humidity conditions is more than sufficient for this purpose.

The principle that is widely used in the construction of direct indicating hopcalite carbon monoxide instruments is the measurement of the heat of reaction by means of differential thermocouples (6, 7). The oxidation of carbon monoxide according to the equation $2\text{CO} + \text{O}_2 \rightarrow 2\text{CO}_2$, liberates 67,960 gm.-cal. per gram-molecule of carbon monoxide and this heat increases the temperature of the gases and components of a reaction cell. If the concentration and space velocity of the reacting gases are maintained constant, a steady temperature state will soon be reached in which the temperature rise indicated or the electric potential generated is a measure of the concentration. Such an instrument, in order to measure rapidly concentrations below 0.01%,

must be capable of accurate and rapid adjustment of the zero reading when operating on carbon-monoxide-free air, and not be subject to appreciable adsorption effects from carbon dioxide or water vapor. Such requirements are not met by the use of hopcalite, except at temperatures of 100°C . or higher, and this produces an undesirable complication in hopcalite instruments, if portability and simplicity of the apparatus are of prime importance.

The above principle has been employed in the present work in the measurement of low gas concentrations by means of the potential generated in a thermocouple cell.

Experimental

The apparatus used in the preparation of the gas-air mixtures and in the measurement of flow rate, and the general arrangement of constant pressure devices, are shown in Fig. 1. The carbon monoxide was prepared by the

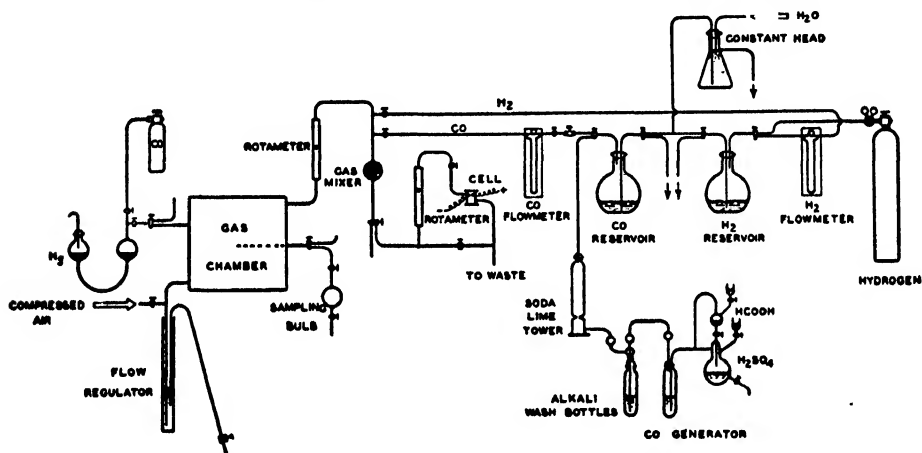


FIG. 1. Apparatus for the preparation of dilute mixtures of carbon monoxide and hydrogen in air, and for measurement of gas flow.

action of formic acid on hot concentrated sulphuric acid in a generator, as shown, and purified by passage through two wash bottles containing 30% potassium hydroxide and a soda lime tower, or, alternatively, carbon monoxide from a high pressure cylinder was used. In experiments where the concentration was maintained constant, the gas was delivered from the carbon monoxide reservoir under a constant head of water and measured by means of a calibrated capillary flowmeter, the manometer height being determined by a cathetometer. Compressed air was used for diluting the gas to the required concentration and was first passed into a gas chamber of volume 26.5 cu. ft. This chamber and the flow regulator enabled a very steady flow to be maintained to the thermocouple cell. The rates of flow from the gas chamber and to the thermocouple cell were measured by calibrated glass rotameter tubes containing aluminum floats. The gas chamber, equipped with mixing fan, was also utilized for the preparation of carbon monoxide - air mixtures in which the initial concentration was decreased at a known rate.

The gas concentrations were determined accurately by collecting instantaneous samples in evacuated glass bulbs of about 500 or 1000 ml. capacity and analyzing a known volume in an iodine pentoxide apparatus shown in Fig. 2. Tube *A* contained granules of the silver permanganate complex and

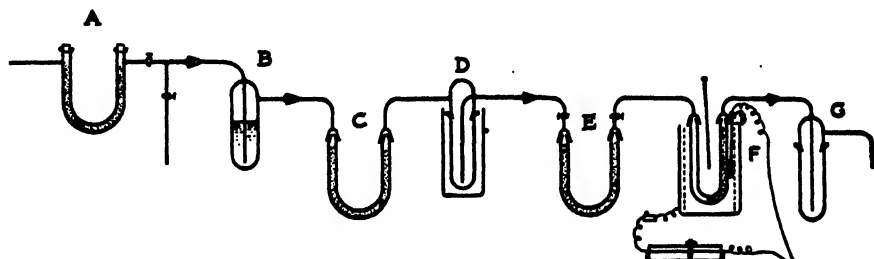


FIG. 2. Diagram of iodine pentoxide apparatus for the analysis of dilute mixtures of carbon monoxide in air.

was used only to pass carbon-monoxide-free air through the apparatus. The sample was admitted at the manifold between *A* and *B*. The bubbler *B* contained concentrated sulphuric acid and was followed by a U-tube, *C*, filled with pumice granules moistened with chromic - sulphuric acid mixture, a liquid air trap, *D*, packed with glass wool, a U-tube, *E*, containing magnesium perchlorate and phosphorus pentoxide, and the iodine pentoxide tube, *F*, maintained in a constant temperature bath at 155° C. The iodine liberated according to the reaction, $\text{I}_2\text{O}_5 + 5\text{CO} = \text{I}_2 + 5\text{CO}_2$ was absorbed in the bulb, *G*, by about 5 ml. of 10% potassium iodide solution and the contents of this bulb was analyzed by titration against standardized 0.002 *N* sodium thiosulphate or sodium arsenite solution (0.005 *N* for the higher concentrations) with a microburette reading to 0.01 ml. Sharp end points were obtained in the titrations with freshly prepared starch indicator. The gas sample was passed through the apparatus at 25 to 40 ml. per min. and the train swept out with carbon-monoxide-free air for about one hour or longer to ensure complete removal of the sample and of the iodine liberated in the reaction. Blank determinations were made on laboratory air, but these were usually negative or at most equivalent to about 5 p.p.m. of carbon monoxide in air by volume.

The granular reagent used in this work was a preparation containing 31 mole % zinc oxide of average particle size about 0.90 mm. The method of preparing this material is described elsewhere (5), but the essential features are uniform deposition of the silver salt on the zinc oxide carrier, pressing of the moist filter cake in a mold at 3 to 5 tons per sq. in., and subsequent air drying of the graded material for 72 hr. at 60° C. Dry samples stored in ordinary brown glass bottles have shown no appreciable diminution in activity towards carbon monoxide after storage for two years at room temperature.

1. Thermal Efficiency

The maximum temperature rise attainable experimentally in the oxidation of carbon monoxide by passing this gas through a simple cell containing

granules of the reagent, and the thermoelectric efficiency, were determined with copper-constantan thermocouples and a Tinsley potentiometer. The cold junctions were maintained at 0° C. in an ice bath.

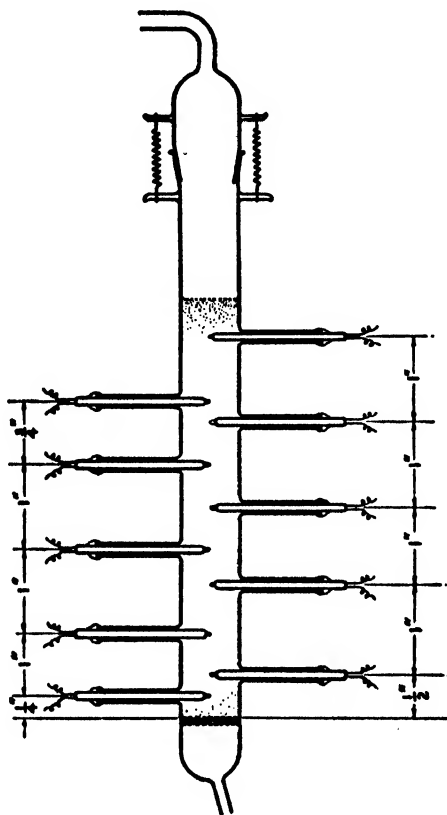


FIG. 3. Diagram of experimental thermocouple cell showing the space arrangement of 10 copper-constantan couples.

The reaction tube, shown in Fig. 3, contained 10 thermocouples embedded at fixed depths, with the hot junctions in the center. The tube was 1.0 in. in diameter and contained a sintered glass disk near the bottom. The gas mixture, under slight pressure, entered at the top and after passing through the bed of granules emerged at the bottom of this tube. The granular bed extended to 0.25 in. above the top thermocouple. The tube was insulated with asbestos.

The average pressure drop between the inlet and outlet ends of this thermocouple cell was determined by a mercury manometer (one end was open to the atmosphere) and cathetometer. At the highest flow rate used in these experiments, about 12 liters per min., this difference was about 15 mm. above barometric pressure.

The maximum temperature rise corresponding to a given set of experimental conditions at constant flow rate, concentration of carbon monoxide, tempera-

ture, pressure, and relative humidity of influent gas, was determined by measuring the potential at various depths in the reaction mass after temperature equilibrium in the system had been attained. The following data were obtained in three experiments in which the concentration of carbon monoxide was maintained at 0.0183% (183 p.p.m.). The temperature of the influent gas mixture was 21.1° C., the average pressure was 778.5 mm., the flow rate 12.1 liters per min., and the relative humidity 30%. (See Appendix A for details of the calculations.)

Theoretically, the heat liberated in the conversion of carbon monoxide to carbon dioxide under the above conditions is 0.5279 gm.-cal. from 183 p.p.m., and the total heat required to raise the temperature of the air, carbon dioxide, and water vapor is 0.298 gm.-cal. per ° C. This gives a theoretical temperature rise of 1.770° C. The above calculations are based on a unit volume of 1 liter of air and carbon monoxide mixture.

The average of the highest potential difference readings found experimentally was 58.0 μ v., and since a single couple gives rise to an e.m.f. of 40.3 μ v. per ° C., the highest temperature rise indicated was 1.439° C. The thermal efficiency is therefore 81.3%. Other experiments at a flow rate of 6.0 liters per min. indicated an efficiency of 65.2%.

At the 12 liter per min. flow rate, the maximum temperature rise was shown by the thermocouples located at 2.25 to 2.75 in. below the surface of the reaction bed, whereas at 6 liters per min. the maximum was reached at a depth of 1.25 to 1.75 in.

2. Relation between Concentration and E.M.F.

The potentials generated in a metal cell containing 55 differential thermocouples (obtained from Mines Safety Appliance Co.) were determined at various concentrations of carbon monoxide in the range of 0 to 600 p.p.m. The cold junction end of the thermocouple cell was filled with inactivated material or granular pumice. The gas mixtures were passed through the cell, which contained 41 gm. or 20 cc. of the reactive granules, at a flow rate of 6.5 liters per min. An instantaneous gas sample was collected in an evacuated glass flask at each potentiometer reading and analyzed by the iodine pentoxide method.

The plot of carbon monoxide concentration in parts per million against the potential in microvolts is shown in Fig. 4. The straight line was drawn after a statistical analysis of the results and indicates a potential of 10.0 mv. at 527 p.p.m. of carbon monoxide.

The potential corresponding to a given carbon monoxide concentration is attained quite rapidly, in about three or four minutes, and on carbon-monoxide-free air the initial zero reading or adjustment may also be made within five minutes. There are no noticeable adsorption effects of water vapor or carbon dioxide.

3. Effect of Gas Flow Rate

At a uniform concentration of carbon monoxide the heat liberated in the reaction cell during oxidation and consequently the potential developed by

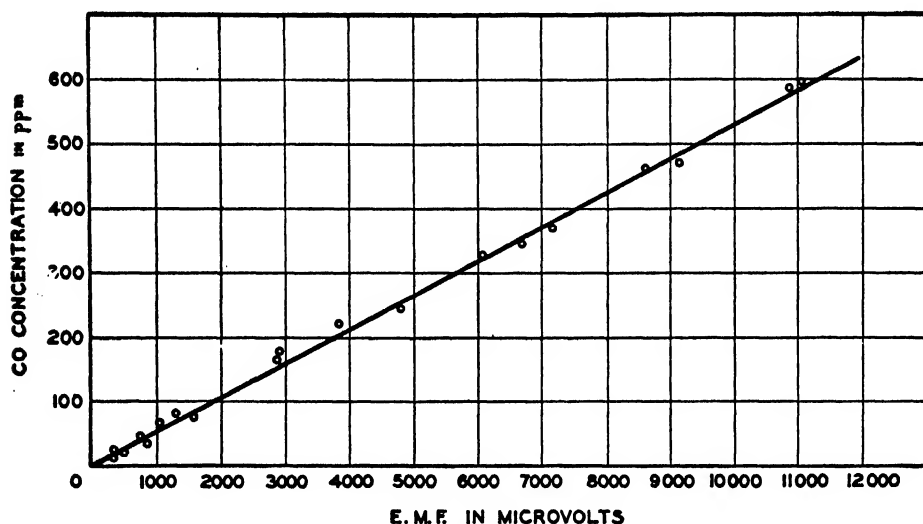


FIG. 4. Relation between e.m.f. and concentration of carbon monoxide in a 55-couple cell. Flow rate, 6.5 liters per min. at room temperature.

the thermocouples will depend upon the flow rate or space velocity. The conversion of carbon monoxide to carbon dioxide is complete at the space velocities used in this investigation.

The effect of increasing the flow rate at various uniform concentrations of carbon monoxide in the multi-thermocouple cell containing 20 cc. of granular material is shown in Fig. 5. The temperature, and consequently the e.m.f., rises until eventually a condition is reached when all the heat generated is dissipated by conduction, by raising the temperature of the gas stream and of the component parts of the cell. When this condition is approached, a relatively large increase in flow rate causes only a small change in potential.

At excessive flow rates, a definite amount of carbon monoxide may pass through the cell without oxidation. On the other hand, when the flow rate is below 6 liters per min., a small variation in flow may cause a large change in potential, especially with high concentrations of carbon monoxide.

The sensitivity or speed of response to carbon monoxide becomes greater at the higher flow rates because the maximum temperature is attained more rapidly. It is desirable in actual practice to strike a balance between all these factors.

4. Effect of Volume of Granule Bed

The effect of increasing the depth of the active bed of granules in the multi-thermocouple cell is shown in Fig. 6. The concentration in these experiments was maintained at 380 p.p.m. of carbon monoxide and the flow rate at 6.5

liters per min. The cell volume was 20.0 cc. and this volume held 41.4 gm. of active material. The depth of bed was varied by filling the unoccupied space with granular pumice of approximately the same size as that of the

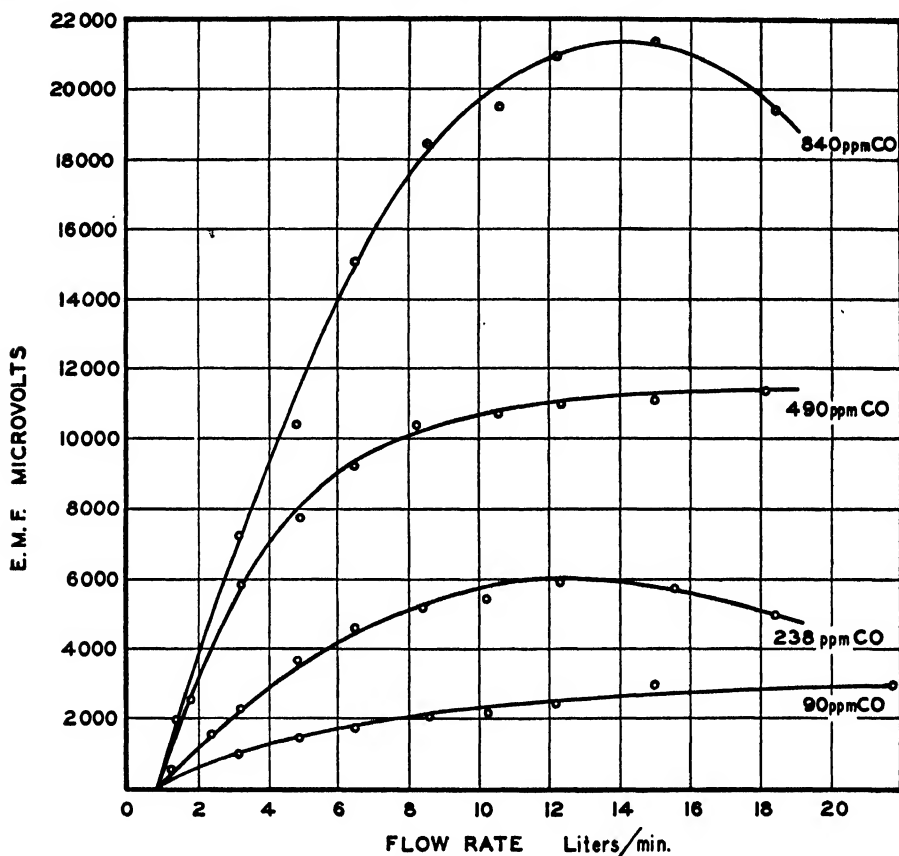


FIG. 5. Effect of flow rate on e.m.f. in 55-couple cell at various gas concentrations.

reagent. When the cell was filled with only a small volume of active material, it was necessary to dispose this layer so as to cover the thermal junctions of the couples and to fill the space above and below this layer with pumice. The size of the reagent bed is given in terms of volume rather than depth because of the variable cross section of the cell.

The potential increased rapidly with increasing volume of reagent until the cell was about half full. Thereafter the potential decreased because the heat was generated in the upper layers of the reacting bed of granules, remote from the thermocouple junctions, and, hence, some heat was dissipated in the intervening layers between the zone of reaction and the junctions.

5. Effect of Hydrogen

The active granules of silver permanganate will oxidize carbon monoxide at a much greater rate than hydrogen at ordinary temperatures. The

influence of successive additions of hydrogen to carbon monoxide-air mixtures is shown in Fig. 7. In these experiments the cell was always filled with 41.4 gm. of material, the flow rate was maintained at 6.5 liters per min., and the gas temperature was about 21° to 23° C.

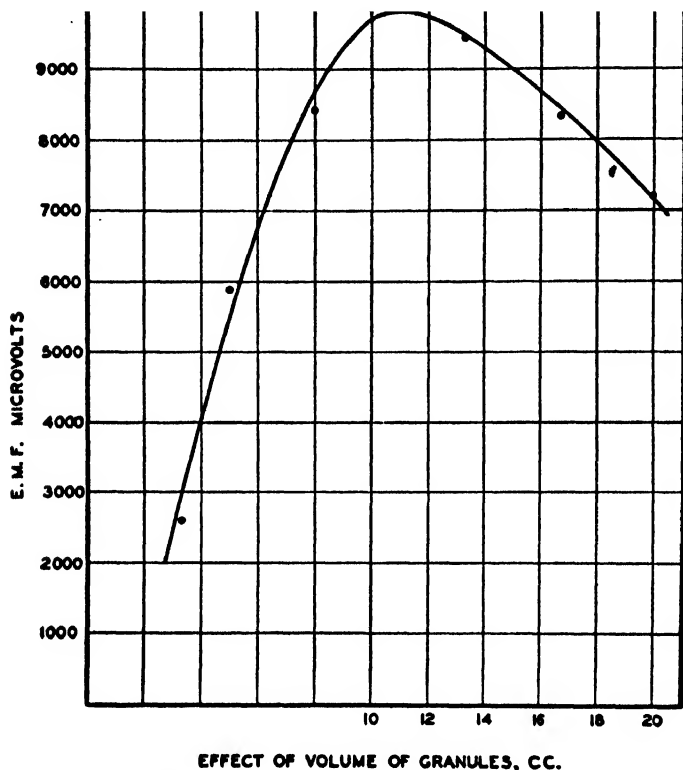


FIG. 6. *Effect of volume of granular silver permanganate bed on potential in thermocouple cell during oxidation of 380 p.p.m. of carbon monoxide at 6.5 liters per min.*

Virtually straight line relations between the concentration and e.m.f. were obtained with successive admixtures of hydrogen up to about 0.5%, when the carbon monoxide concentration was varied from 75 to about 700 p.p.m. The e.m.f. was increased only slightly by the presence of hydrogen. Thus, in the absence of carbon monoxide, about 0.5% hydrogen in air at the above flow rate showed a small temperature rise equivalent to a potentiometer reading of 700 μ v.

If a gas mixture contained twice as much hydrogen as carbon monoxide, for example, 0.06% carbon monoxide and 0.12% hydrogen, and if the apparatus were calibrated for carbon monoxide only, the error in the reading would be about 1.3%. For practical purposes, the influence of hydrogen on the carbon monoxide calibration curve may be neglected under the usual conditions of measurement in a contaminated atmosphere. The gases

liberated from the incomplete combustion of fuels or exhaust gas from internal combustion engines usually contain much less hydrogen than carbon monoxide.

6. Relative Humidity and Temperature of Gas Stream

In the range of about 30 to 100% relative humidity of the air, the combustion of carbon monoxide on the surface of these granules is equally efficient

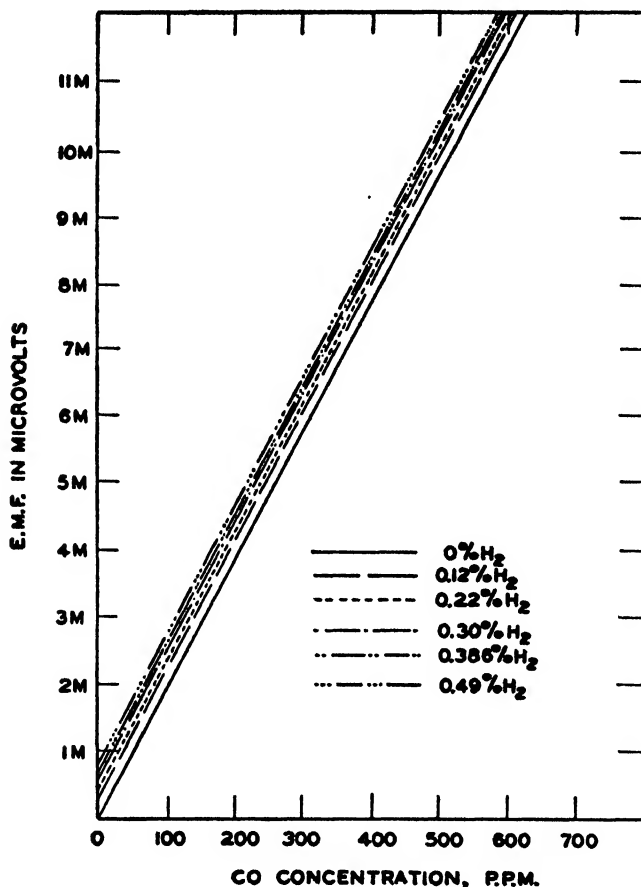


FIG. 7. Effect of hydrogen on the relation between e.m.f. and carbon monoxide concentration. Gas flow through thermocouple cell, 6.5 liters per min. at room temperature.

and a single calibration curve will suffice. However, with air mixtures of very low humidity, i.e., less than 20%, the rate of oxidation is influenced by an induction period. Furthermore, the granules are almost inactive in completely dry air. In such instances the necessary humidity may be imparted to the gas stream by passing the sample through a small bubbler of water.

The experimental data discussed thus far were obtained at room temperature, 21° to 23° C., but the material may be used just as effectively at higher

temperatures up to 60° C. Beyond this temperature the velocity of decomposition of the silver permanganate becomes appreciable and this limits the active life of the granules.

At low temperatures the activity of the material decreases quite rapidly from 0° to -20° C. About 95 to 97% of the carbon monoxide, in an air stream containing 0.5%, is oxidized to carbon dioxide at 0° C. at a space velocity of 800 cc. per cm.² per min., but the life of the granules is reduced to about 50 to 60% of the value at room temperature.

The method is therefore not suited to the measurement of carbon monoxide at low temperatures unless the granular material is maintained at temperatures above 0° C. by a heater unit. In a number of experiments in which the gas stream was cooled to -20° C. or lower by passage through a cooling coil immersed in solid carbon dioxide and acetone, or liquid air, the temperature rise in the thermocouple cell was of the right order of magnitude as long as the mass of solid reagent was not cooled to the temperature of the influent gas.

7. Active Life of Granules

The zinc oxide-silver permanganate granules eventually lose their capacity to oxidize carbon monoxide on prolonged exposure, owing to the irreversible depletion of oxygen from the silver salt during the progress of the stoichiometric reaction. The active life, at ordinary temperature and relative humidity, is determined by the concentration and space velocity of the gas mixture, the time of exposure, and the volume or column length of the bed of granules.

If it is assumed that the material in the thermocouple cell must be replaced when the efficiency of oxidation falls to 99%, then a bed of 25.0 cc. volume and depth of 5.0 cm. will have an active life of over eight hours of continuous service if a gas mixture containing 0.10% carbon monoxide is passed through it at a space velocity of 800 cc. per cm.² per min. Under less rigorous test conditions the service life would be proportionately longer.

An indicating instrument for the determination of physiologically significant concentrations of carbon monoxide in contaminated air would normally be used on intermittent test periods over the range of 0 to about 500 p.p.m. Under such conditions the cell would not need to be refilled with fresh granules until the total exposure amounted to about 16 hr.

Discussion

The oxidation of carbon monoxide at ordinary temperatures by silver permanganate deposited on a zinc oxide carrier has been utilized in a rapid method for the determination of low concentrations of carbon monoxide. With a conventional multi-thermocouple cell and a potentiometer that will measure e.m.f. to 1 μ v., the concentration may be determined to within a few parts per million. Results accurate to 5 p.p.m., in the range of concentration from 10 to 200 p.p.m., have been obtained by measuring the e.m.f. with a Universal Polyrange.

The granules possess adequate hardness and may be graded to $-14, +20$ mesh for use as an indicator material. The carbon monoxide measurements are reproducible during the active life of a given quantity of material. While a small amount of water vapor is necessary to initiate oxidation, the relative humidity of the gas stream may be increased from 30 to 100% without any noticeable change in the calibration curve. The temperature equilibrium corresponding to a given carbon monoxide concentration is attained rapidly, usually within four minutes.

The thermoelectric measurements indicate a linear relation between concentration and potential. With increasing flow rate at a uniform gas concentration, the potential rises rapidly at first but more slowly thereafter so that relatively large variations in flow rate have only a small influence on the e.m.f. in this region. The volume of the granular bed must be maintained constant in a given thermocouple cell, as variations in the depth of bed may cause major changes in potential. With increasing depth of bed the potential curve at constant gas concentration and flow rate passes through a maximum.

Hydrogen may be present in the gas mixture in amounts considerably in excess of that of the carbon monoxide without introducing an appreciable error in the determination. The concentration of hydrogen in the combustion products of fuels is usually less than that of the carbon monoxide.

The special properties of these silver permanganate granules, in particular their stability in the presence of water vapor and their freedom from adsorption and poisoning effects, make this oxidant eminently suitable for the rapid determination of low concentrations of carbon monoxide in aircraft, motorized vehicles, mines, and buildings where the air is likely to be contaminated by this gas.

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Appendix A

Calculation of Maximum Thermoelectric Effect in Thermocouple Cell during Oxidation of Carbon Monoxide

The calculations are based on a unit volume of 1 liter of air and carbon monoxide mixture at $21.1^{\circ}\text{C}.$, an average pressure of 778.5 mm. within the cell between the inlet and outlet ends (Fig. 3), a concentration of 0.0183%,

and a relative humidity of 30%. The specific heats, or C_p values, have been obtained from data in the Handbook of Physical Constants, Geological Society of America, 1942.

Gas	Density at 21.1° C. and 778.5 mm., gm./liter	Specific heat, C_p at 21.1° C., cal./gm.
CO	1.1886	—
CO ₂	1.8797	0.19895
Air	1.2293	0.24053
H ₂ O vapor	—	0.44354

Heat of combustion, carbon monoxide to carbon dioxide = 67,960 gm.-cal. per gram-molecule, or 2,427 gm.-cal. per gm.

Mass of carbon monoxide in grams per liter = $1.1886 \times 0.000183 = 0.0002175$

Mass of water vapor in air at 30% relative humidity, in grams per liter = 0.005445

Heat liberated during oxidation of 0.0183% carbon monoxide
 $= 0.0002175 \times 2427$
 $= 0.5279$ gm.-cal.

Heat required for the carbon dioxide
 $= 1.8797 \times 0.000183 \times 0.19895 = 0.00006843$ cal. per °C.

Heat required for the air = $1.2293 \times 0.24053 \times 0.9997 = 0.2957$ cal. per °C.

Heat required for the water vapor = $0.005445 \times 0.44354 = 0.002415$ cal. per °C.

Total calories per degree Centigrade for the carbon dioxide, air, and water vapor = 0.298183

Theoretical temperature rise = $\frac{0.5279}{0.29818} = 1.770^\circ \text{C.}$

One copper-constantan couple was found, experimentally, to yield an average e.m.f. of 58.0 $\mu\text{v.}$ during the oxidation of 0.0183% carbon monoxide, and since this couple indicates a potential of 40.3 $\mu\text{v.}$ per °C., the temperature rise measured actually was 1.439° C.

Percentage of theoretical temperature rise attained in cell

$$= \frac{1.439 \times 100}{1.770} = 81.3.$$

PHOTOMETRY AND COLORIMETRY OF RAILROAD FUSEES¹

By W. E. KNOWLES MIDDLETON

Abstract

In connection with the preparation of a standard specification, it became necessary to investigate the luminous intensity and color of a large number of railroad fusees. The rapid and wide fluctuations in intensity made it necessary to use special methods of colorimetry. The intensity was recorded by a high-speed electronic potentiometer and a barrier-layer photocell with correcting filter. To the pen carriage of the potentiometer was attached a special diaphragm which, with a lens and slit, acted as a 'light valve' to keep the flux into the colorimeter at a constant level over a range of about four to one. The very rapid flickering was, of course, not entirely eliminated. Visual colorimetry was used, the comparison field being produced in the lower half of a divided integrating sphere, the upper half of which received light from the fusee under test. The field, 2° in diameter, could be observed with both eyes. The accuracy of the colorimetry was made adequate by a careful choice of filters, advantage being taken of a fortunate circumstance regarding the color of the fusees. The results of testing more than 200 fusees are summarized.

Introduction

As part of the ground work for a comprehensive specification for the safety fusees used by the Canadian railways, the writer was asked to measure the intensity and color of the light from a large number of fusees, and to make recommendations based on the data obtained. No particular problems arise in the photometry of such sources, but the colorimetry of a flame that flickers violently is by no means easy, and it is felt that the methods used may be of general interest.

The fusees used by the Canadian railways are of two colors, red and yellow. They consist of a suitable composition packed into a rolled paper tube (sometimes reinforced by a layer of textile material), sealed by a removable cap having a safety match composition on its end, which is used to light the fusee. A spike at the lower end of the fusee is supposed to stick in the tie or ballast when the fusee is dropped from the rear platform of the train. All Canadian fusees have a nominal burning time of 10 min.

Photometry

The fusee was burned in a fume cabinet, and its intensity in a specified direction was continuously recorded by a photometer consisting of a barrier-layer photocell and a Brown 'electronic' potentiometer of the high-speed type. This gave a satisfactory record of the fluctuations in the light from the fusee. The photocell was provided with a filter that made its spectral sensitivity match the luminosity curve of the normal eye very closely. A sample record is shown in Fig. 1. The time-scale gives an automatic record of the burning

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time, while the mean candle power can be found by estimation or with a planimeter.

It was decided to burn all fusees at an angle of 20° to the vertical in the plane containing the photocell, and pointing away from it. The large fluctuations in the light are due mainly to 'chimneying', the formation of a tube of slag that partly hides the flame, and may reduce the light almost to zero before it breaks away.

The mean intensity of the fusees varied from about 150 candles to less than 50. Short bursts of over 250 candles were fairly common.

Colorimetry

The modern tendency in the colorimetry of light sources is to use photo-electric methods with three or four filters, such as have been described by Barnes (2). With such a variable source as a fusee, however, it would be necessary to make simultaneous and instantaneous measurements with all the filters. This would involve three or four photocells (probably photo-emissive cells), three or four special filters, and an equal number of cathode-ray oscilloscopes and cameras, or similar apparatus. Small but important fluctuations in color, not serious in themselves, seemed to rule out the alternative method of measuring the relative responses of three or four filters two at a time. Since the problem did not seem to warrant, nor time permit, the development of the special filters required, it was decided to forego photo-electric methods.

This left (a) photographic spectroradiometry and (b) visual colorimetry. Fig. 2 shows the spectra of typical red and yellow fusees, the strontium, potassium, and sodium lines being easily recognizable features. Note that there is little energy at wave lengths less than 5889 \AA , but the barium lines are visible in the spectrum of the yellow fusee. In view of the large number of fusees that had to be tested and the tediousness and difficulty of the photographic method, visual colorimetry was rather reluctantly decided upon. As it turned out, a number of fortunate circumstances combined to reduce the difficulty of this method for the particular fusees in question.

Apparatus

The apparatus, shown diagrammatically in Fig. 3, consisted of four main parts:

(A) A mechanism for keeping the flame on the center line of the optical system,

(B) The barrier-layer photocell referred to above,

(C) A 'light-valve' operated by the Brown potentiometer, and a lens to form an image of the flame on the wall of

(D) A sphere, internally whitened with magnesium oxide, and divided into two hemispheres by a horizontal whitened plate. Light from the fusee enters the upper hemisphere, while into the lower hemisphere light is sent from



FIG. 1. *Photometer record of red fusee.*

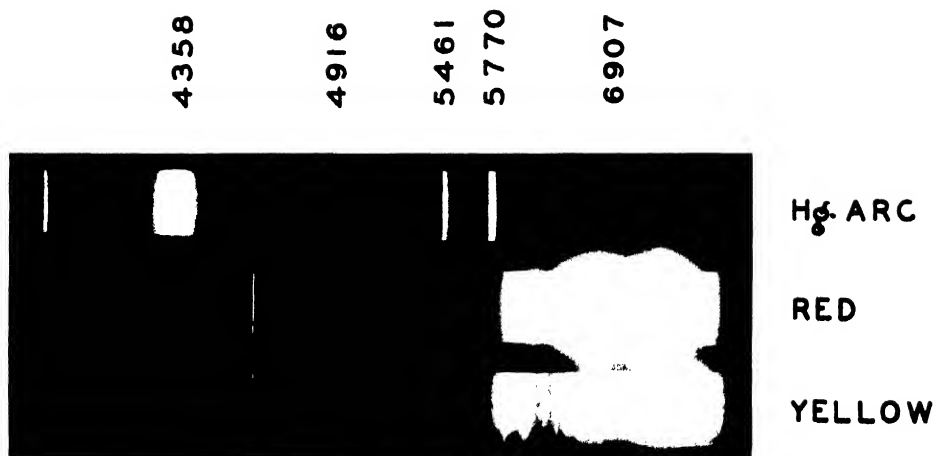


FIG. 2. *Spectra of red and of yellow fusees, with mercury arc spectrum for comparison.*

(E) A color-mixing device consisting of a lamp, a condensing lens, and three sectors of variable angle, provided with red, green, and blue filters, respectively. This part of the apparatus is very similar to the corresponding part of the

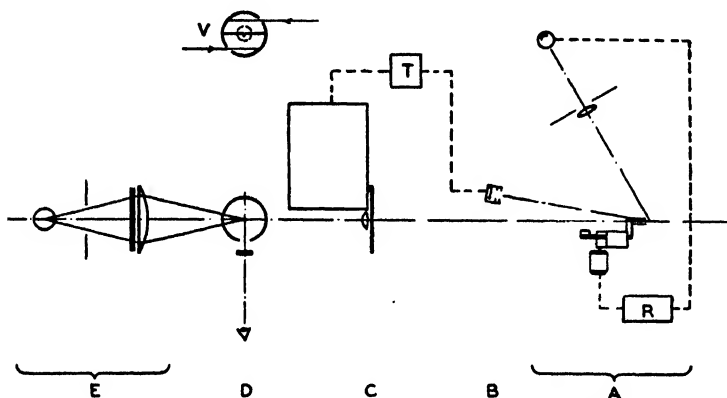


FIG. 3. General arrangement of apparatus. A, B, C, D, E, see text; R, thyatron relay circuit; T, decade resistance box; V, vertical section through sphere.

Donaldson colorimeter (3), except that sectors were used instead of slides. In addition, a small source of blue light was provided for desaturating the light from the fusee.

This apparatus, which will now be described in more detail, was by no means of permanent construction, being set up entirely for these tests. Nevertheless, a good deal of care was taken with the essential parts, especially the sectors.

The mechanism A is shown in Fig. 4, and consists essentially of a holder for the fusee, mounted on a nut that is driven up or down a screw by a reversing motor. The screw is inclined at an angle of 20° to the vertical. When an image of the flame is thrown by a lens on to a photocell, a relay closes and causes the motor to raise the fusee until the image just clears the photocell slit. This action is repeated every few seconds during the time of burning, the flame being kept satisfactorily centered on the optical axis. The motor is reversed by a manual switch at the end of the run. Limit switches are provided. The screw is surrounded as completely as possible by sheet steel in order to protect it from the molten slag, which is projected in all directions.

The light valve C is shown in Fig. 5. It consists of a light aluminum structure with two opposed curved edges, mounted on the pen carriage of the Brown potentiometer. Just behind this is mounted a vertical slit about 1 cm. wide, and a positive lens that forms an image of the fusee flame on the opening in the upper half of the sphere D. Acting together, the vertical slit and the aperture with curved edges form a stop for the lens, of which the area is approximately inversely proportional to the deflection of the potentiometer, and thus to the illumination of the photocell B. In this way the general level of brightness in the upper half of the sphere is kept fairly constant as long as

the intensity of the fusee does not fall below about 50 candles. The potentiometer does not, of course, follow the rapid flickering of the flame, but the maintenance of an approximately uniform brightness in the sphere makes colorimetry possible.

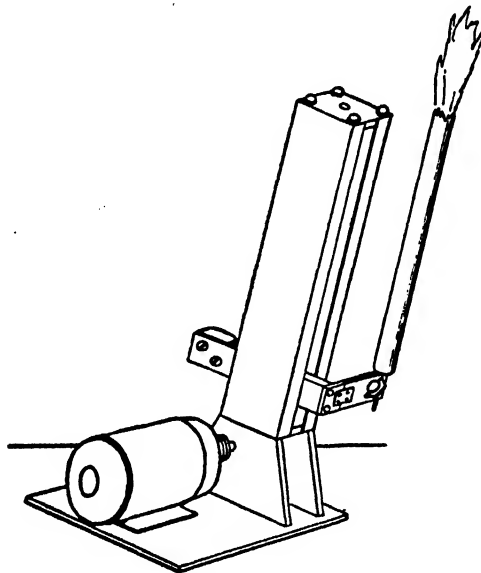


FIG. 4. *Automatic fusee holder.*

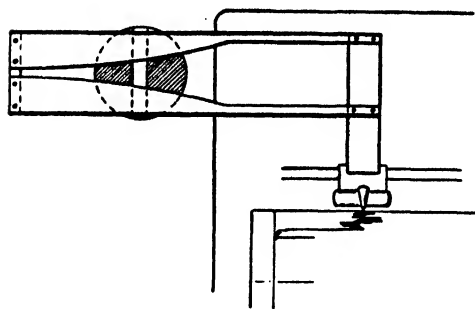


FIG. 5. 'Light valve'. *The sketch of portion of the recording potentiometer is purely schematic.*

The sphere *D* needs little further description, except to note that a double prism of narrow angle is used to make the dividing line inconspicuous. The two-part circular field that results is observed binocularly from such a distance that its angular diameter is about 2° . The possibility of binocular observation is a great comfort in the difficult task of matching the color of the flickering flame*, and indeed dictated the general design of this part of the apparatus.

The color-mixing device is completely conventional. The lamp is a 500 w. projection lamp operated at the temperature of I.C.I. source 'A' on alternating

* A somewhat similar use of a divided sphere has been described by Van den Akker (7).

current regulated to 0.1 v. The filters are Wratten 70 for the red, Wratten 74 for the green, and Wratten 49B for the blue. A 40%, neutral filter is used behind the green filter to give better scale readings.

As it was obvious that blue would be the only color needed for desaturation, a small projector was provided, run from a storage battery, in lieu of the complications involved in getting the desaturating light from the main source.

The apparatus was carefully screened to exclude stray light, but the screens have not been shown in Fig. 3.

Calibration

The calibration followed the usual procedure (6; 8, p. 103), except that the scales of the color-mixing apparatus were calibrated with a photoelectric photometer that reads on a potentiometer of great accuracy. An observer with approximately normal color vision was selected to make the routine observations, and each morning he first made at least three matches on source 'A' (substituted for the fusees), from the average of which the conversion equations for the day were calculated.

In order to show the necessity of this routine, Fig. 6 is presented. The points in this figure were calculated as follows. The ratio of green to red

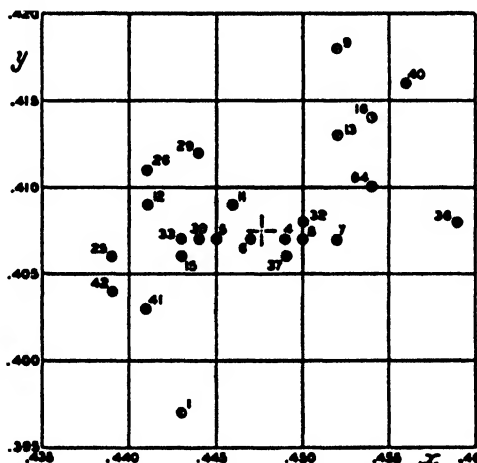


FIG. 6. Variations in color vision of the observer (see text).

(corrected sector readings) in the match on source 'A' was written down for each of the 24 days on which color measurements were made, and the mean value taken. Using the conversion equations for a day on which the green-red ratio was near this average, the color of source 'A' was calculated from the mean of each day's settings. The figures beside each point represent the elapsed time in days from the first measurement, this being counted as Day 1 (Dec. 5, 1947). The cross shows the co-ordinates of source 'A' as officially defined. Apart from the fact that Day 1 is displaced towards purple, there seems to be no trend in the observations, and even Day 64, representing a

match made after an interval of 22 days during which the observer did no colorimetry, is well within the general variation. If we ascribe the result for Day 1 to unfamiliarity with the apparatus, the remaining points may be considered to represent the variation in the color vision of the observer from one day to another.

The question is now whether this variation is properly compensated by the technique of making a daily match on source 'A'. If it were not, we should expect some correlation between the values of y , say, plotted in Fig. 6, and the corresponding means of the y -values for the red fusees measured on the days in question. The correlation coefficient between these quantities, calculated by the product-moment method, is $+0.02$. If we confine the sample to the days before number 26, including only fusees less than three years old, the coefficient of correlation is -0.03 . Since these coefficients are negligible, it appears that the technique of matching source 'A' each morning does actually compensate almost completely for the variations in the color vision of the observer.

The trichromatic co-ordinates of the filters, used with I.C.I. source 'A', were determined with a recording spectrophotometer, and are as shown in Table I.

TABLE I

Filter	x	y	z
Wratten No. 70 (Red)	0.7322	0.2678	0.0000
" " 74 (Green) + Neutral 40%	0.2125	0.7518	0.0357
" " 49B (Blue)	0.1506	0.0264	0.8230

These colors are plotted on the standard I.C.I. chromaticity diagram in Fig. 7, and it will be seen that the green filter is much yellower than one would choose for general colorimetry. This has the advantage that all mixtures of red and green from the filters are of high saturation.

Colorimetric Procedure

Five matches were made on each fusee, spaced about two minutes apart during the 10 min. available. At first a small amount of blue light was added to the light from the fusee, which was itself always more saturated than any mixture of the three filter colors; but great difficulty was experienced in deciding on the amount of blue to use in the extremely awkward match between the flickering light from the fusee and the steady light in the lower part of the field. There was little uncertainty in the relative amounts of red and green to be used, and, when the results of a number of matches on red fusees were plotted, they all lay close to a line that, if produced, would pass through the point representing the blue filter. A similar line was obtained for the yellow fusees. At the same time the observer felt unhappy about the entire procedure.

At this point it was noted that the color of the fusees could be restricted to a very small region of the diagram with almost complete certainty (especially in the case of the red fusees) by operating without any desaturating light and making use of the observation that the color of the light from the fusee was always more saturated than that produced with the red and green filters alone. This reduced the colorimetry to a two-dimensional problem, and located the colors in small regions between the line $R-G$ and the spectrum locus (Fig. 7). A careful watch was kept for fusees giving a light less saturated than the mixture of red and green, but without success except for one or two red fusees more than 30 years old, which were just doubtful.

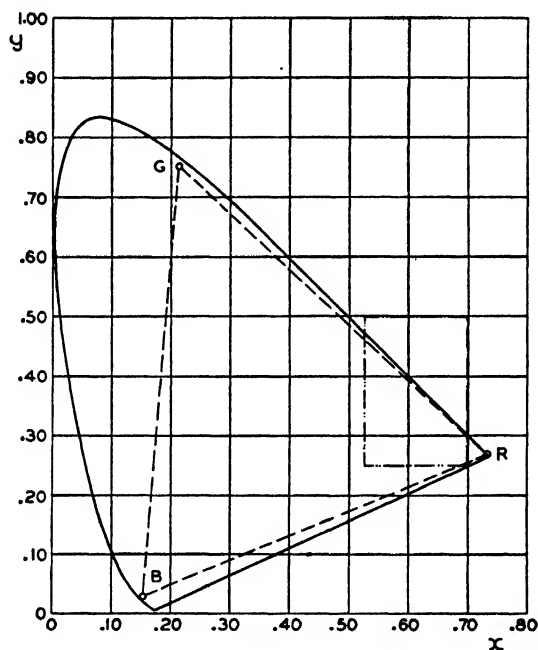


FIG. 7. I.C.I. chromaticity diagram, showing the spectrum locus and the chromaticity of the three colors used in the colorimeter. The rectangle in dashed lines shows the portion of the diagram included in Fig. 7.

Results of Colorimetry

The main results of the colorimetry are shown concisely in Fig. 8, which represents that portion of the chromaticity diagram within the small rectangle in Fig. 7. A portion of the spectrum locus, and of the line $R-G$, will readily be identified.

As mentioned above, the colors of all the fusees certainly lay between the line $R-G$ and the spectrum locus. The mean of five observations on a fusee gave a probable error in y of the order of ± 0.002 . The colors are therefore represented by quadrilateral figures, cross-hatched in Fig. 8, within which the central 90% of each type lay. When it is considered that these fusees were manufactured over a period of more than 30 years, the constancy in

color is remarkable. If any two red fusees, selected at random, had been burnt side by side and observed from a considerable distance, it is unlikely that any difference in color would have been perceived.* The yellow fusees show scarcely any more variation. It is true that all the fusees in question were of the same manufacture, but tests on a small number of recent fusees from about 10 different sources in the United States showed only slightly greater differences. None of the latter, incidentally, gave colors less saturated than the combination of the red and green filters.

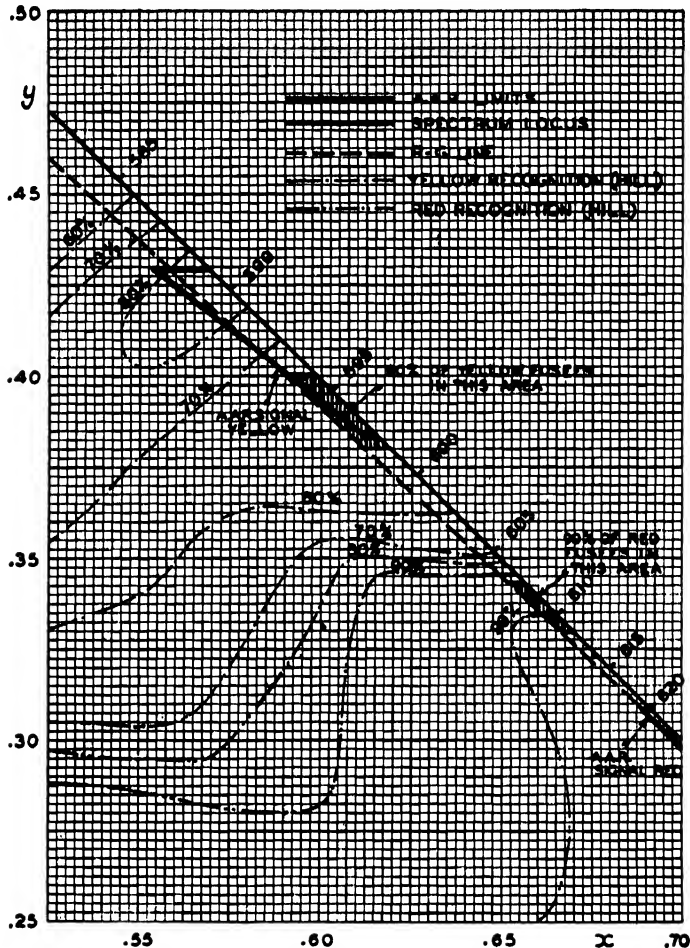


FIG. 8. Portion of the chromaticity diagram, greatly enlarged.

In order that the probable appearance of these colors may be determined, some curves obtained by Hill (4) have been plotted in Fig. 8. These curves show the percentage of times that an observer with normal color vision will

* The writer knows no data relating to point sources that would permit a more positive statement than this.

distinguish a given color at night when it is viewed as a point source and produces an illumination of 2 lumens per square mile at the eye. Nearly all the red fusees will be judged red under these conditions more than 90% of the time. For the yellow fusees the situation is not nearly as satisfactory; indeed, they might all be frequently mistaken for red. Since the effect of haze and smoke is almost* invariably to make composite yellow lights look redder, there might be many conditions when a yellow fusee for which $y = 0.385$ or thereabouts would be red to an observer at a distance. Since red means 'stop', such a misinterpretation would, of course, be on the safe side.

For comparison, the A.A.R. (1, p. 3) signal limits are shown in Fig. 8 by double outlines. The red limits extend beyond the drawing to the end of the spectrum.

The color of the red fusees would be described as 'reddish orange' on the N.B.S. system of naming light sources (5).

Conclusion

The writer hopes that this paper may draw attention to the fact that visual colorimetry, an unpopular procedure on this continent, may still be useful under special circumstances. The calibration of a trichromatic colorimeter, at least, ought to be part of the education of every colorimetrist for the insight it gives into the properties of the mixture diagram; this is written with no intent to minimize the possible errors of visual colorimetry.

The technique described in this paper is obviously not suited to the routine examination of fusees for color. Work on a suitable test is in progress.

Acknowledgment

The writer wishes to thank Mr. W. A. Newman, Manager of the Department of Research, Canadian Pacific Railway Co., for making the necessary arrangements for the supply of fusees and for liaison with the manufacturers.

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* The qualification recognizes the peculiar selectivity of steam under certain conditions, but is of little practical importance.

GRAPHICAL ANALYSIS OF CATHODE COUPLED AMPLIFIERS¹

BY HUGH A. WATSON

Abstract

A graphical means of design and gain calculation for cathode coupled amplifiers is described. The method, based on data supplied by the plate characteristic curves of the tube, can be used to advantage in predicting the performance of the amplifier and in determining the zero signal operating conditions.

Introduction

A number of papers have recently appeared in the technical publications on the characteristics and applications of cathode coupled twin triode amplifiers. Evidence has been given that these amplifiers can be designed to have a gain comparable to that of a pentode for radio frequency or video amplification purposes. It has further been pointed out that less grid noise is apparent in their output, that the twin triode with common cathode is cheaper to construct than a pentode of equal transconductance, and that the elimination of a screen supply dropping resistor and by-pass capacitor makes the stage more compact. These advantages, coupled with large bandwidth properties, have resulted in cathode coupled amplifiers finding increasing use where video gain is required.

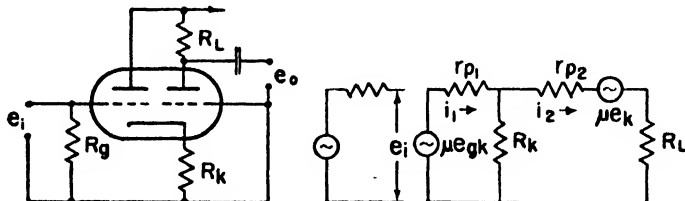


FIG. 1. Cathode coupled amplifier and equivalent network.

The basic circuit is shown in Fig. 1. A cathode follower unit drives a second stage operating as a triode with grounded grid. For purposes of analysis it must be assumed that the zero signal potential of the grid of the first unit is that of ground, or is biased at a known potential relative to ground.

Graphical Design

Starting with a set of plate characteristics for the twin triode and assuming a load resistance, R_L , and supply voltage, E_b , a suitable bias, E_{gk2} , for the second unit is chosen. This is supplied by the cathode resistor. The bias for the first unit, E_{gk1} , will be the sum of this and any additional externally applied bias. Two curves are then drawn on the sheet of plate characteristics. Curve 1 is a vertical line intersecting the voltage axis at $E_b - E_{gk2}$. Curve 2

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is a line having a slope corresponding to the plate load resistor and intersecting the voltage axis at the same point as Curve 1. These curves represent graphically the relation between plate current and plate-to-cathode voltage for the first and second units, respectively. No account is taken of the variation in cathode potential, as usually it is of the order of less than half a per cent of the plate-to-cathode voltage.

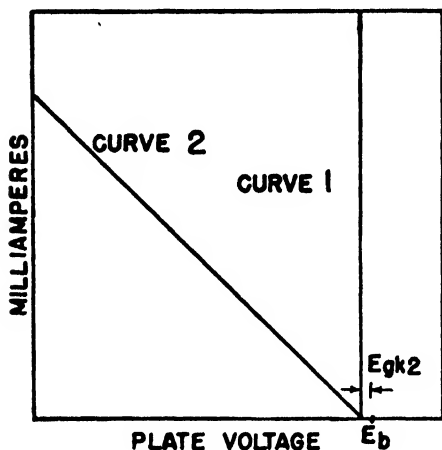


FIG. 2. Curves 1 and 2.

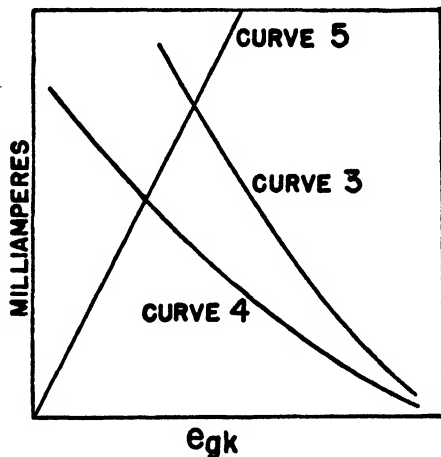


FIG. 3. Curves 3, 4, and 5.

The value of the cathode resistor is found by dividing the voltage E_{gk2} by the sum of the zero-signal currents drawn by the two units. The zero-signal current drawn by the first unit is found from the intersection of Curve 1 and the plate characteristic corresponding to the bias, E_{gk1} , assumed for that unit. The zero-signal current drawn by the second unit is found from the inter-

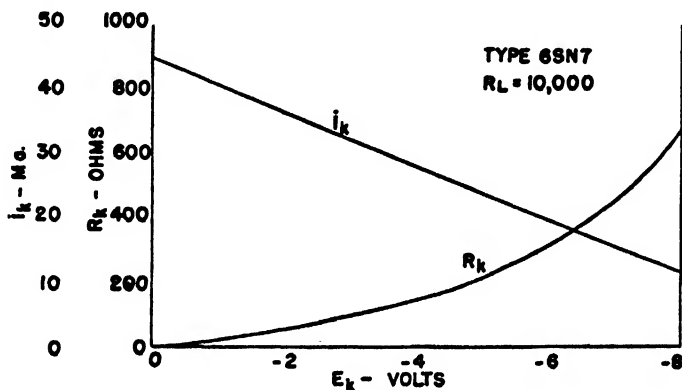


FIG. 4. Cathode resistor and current values.

section of Curve 2 and the plate characteristic for E_{gk2} . Fig. 4 shows the resistor values required for various bias voltages in the case of a 6SN7 with 250 v. plate supply.

illustrate three complete amplifier designs with all curves drawn in place. The first unit of each amplifier has no additional bias applied, as it is not required in most applications.

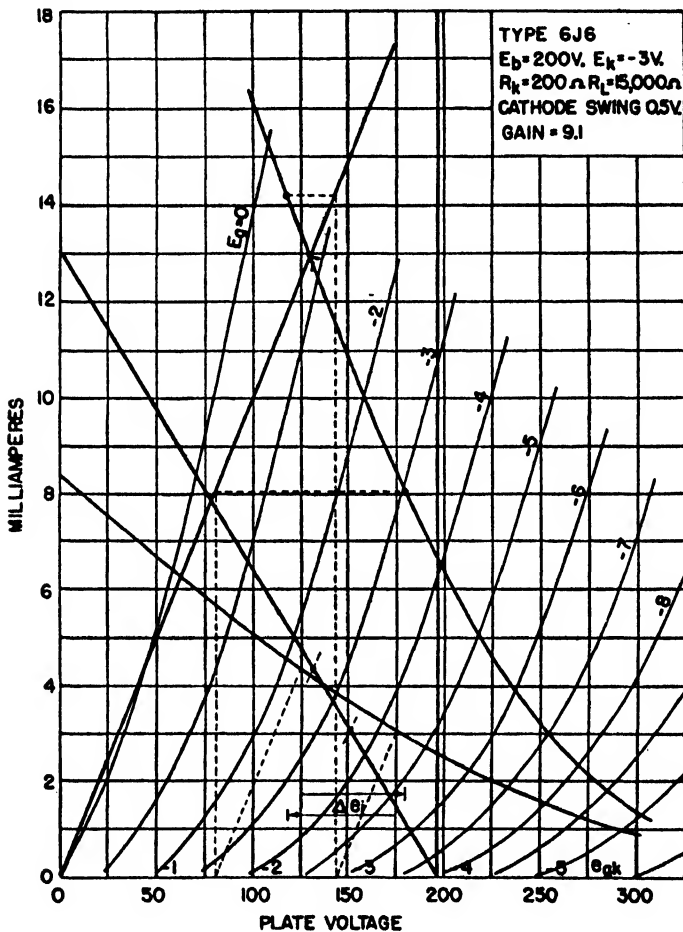


FIG. 6. Work sheet for a 6J6 amplifier.

To determine the gain, a small swing in cathode voltage is assumed. The points $O_1 - A_1$ corresponding to this swing are shown on Curve 2 of Fig. 5. Here the zero-signal cathode voltage, E_k is -6 v., and an applied signal causes it to swing to -5 v. The output swing, about -11 v., is read as the difference in the abscissae of the points. On Curve 4 point A_1 becomes A_2 , the ordinate of the points being the current drawn by the second unit. However, point B on Curve 5 gives the sum of the currents in the two units and the difference A_2B must be the current drawn by the first unit. The broken lines show a geometrical construction for finding point C on Curve 3 corresponding to this current. The abscissa of C , namely, -7.6 v., gives the grid-to-cathode voltage necessary for the unit to draw this current. The

voltage drop across the cathode resistor is given by the abscissa of point A_2 , viz., -5 v. and the difference, -2.6 v., must be supplied by the input signal. This difference is shown as Δe_c in the diagrams. Thus the gain is $\frac{-11}{-2.6} = 4.2$, approximately. If any additional fixed bias had been applied to the first unit, this would have to be subtracted from the -2.6 v. in order to obtain the input signal.

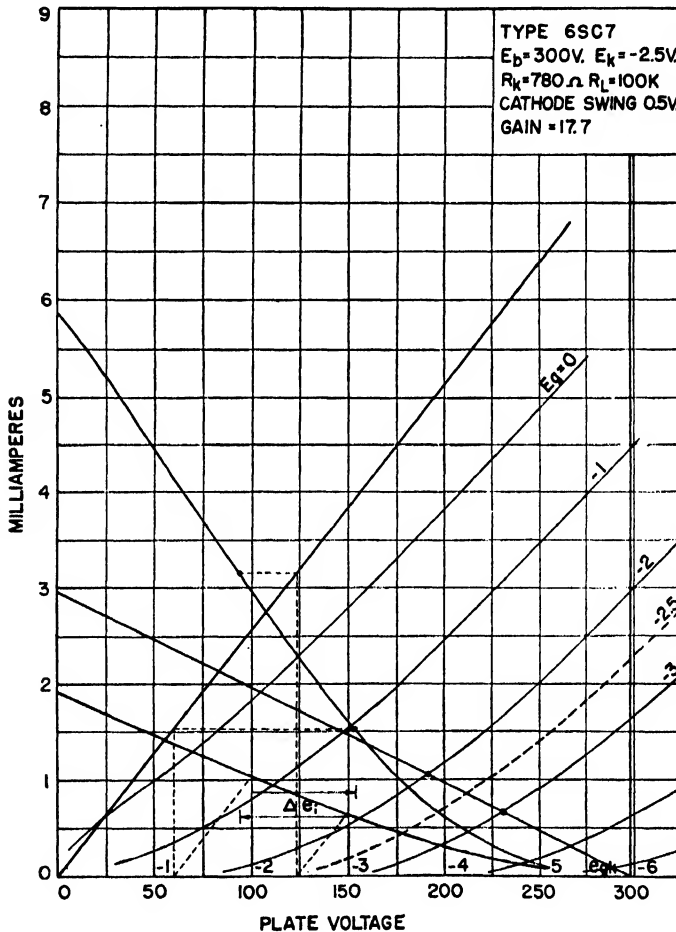


FIG. 7. Work sheet for a 6SC7 amplifier.

An equal and opposite swing in cathode voltage should be investigated in a similar manner and results compared. If all voltages are symmetrical it may be assumed that little distortion is produced by the amplifier. If they are not equal, a lower cathode bias should generally be tried and a new calculation made.

It will be noted that the plate currents in the two units are out of phase and hence subsequent similar units have little effect on each other owing to supply

voltage variations. We also find that the output voltage is in phase with the input.

Theoretical Gain

The equivalent circuit of the cathode coupled amplifier is shown in Fig. 1. Here the instantaneous plate currents in the two units are represented by i_1 and i_2 , respectively, and the two plate resistances are represented by r_{p1} and r_{p2} , respectively. The instantaneous input voltage is denoted by e_i , and the instantaneous voltage across the cathode resistor, R_k , is denoted by e_k . R_L is the plate load resistance for the second unit. The symbol e_{gk} is used to denote the grid-to-cathode voltage for the first triode only. The left-hand loop of the network corresponds to the first triode and the right-hand loop corresponds to the second triode.

Since the sum of the voltages around the left-hand loop must be zero, we may write:

$$i_1 r_{p1} + (i_1 - i_2) R_k - \mu e_{gk} = 0. \quad (1)$$

$$\text{But } \mu e_{gk} = \mu (e_i - e_k) = \mu e_i - \mu (i_1 - i_2) R_k \quad (2)$$

therefore

$$i_1 [r_{p1} + R_k (\mu + 1)] - i_2 [R_k (\mu + 1)] = \mu e_i. \quad (3)$$

Similarly for the second loop we obtain:

$$(i_2 - i_1) R_k + i_2 (r_{p2} + R_L) = \mu e_k = \mu (i_1 - i_2) R_k, \quad (4)$$

from which

$$i_1 [R_k (\mu + 1)] - i_2 [r_{p2} + R_L + R_k (\mu + 1)] = 0. \quad (5)$$

Solving for i_2 from (3) and (5) we obtain:

$$i_2 = \frac{\mu e_i R_k (\mu + 1)}{r_{p1} r_{p2} + r_{p1} R_L + (r_{p1} + r_{p2} + R_L) R_k (\mu + 1)}. \quad (6)$$

Hence the gain produced by the amplifier is given by

$$\frac{i_2 R_L}{e_i} = \frac{\mu R_L R_k (\mu + 1)}{r_{p1} r_{p2} + r_{p1} R_L + (r_{p1} + r_{p2} + R_L) R_k (\mu + 1)}. \quad (7)$$

Using this expression, the theoretical gains of the amplifiers shown in Figs. 5, 6 and 7, are tabulated below, together with the results obtained graphically and experimentally:

Type	R_k	R_L	r_{p1}	r_{p2}	μ	Theoretical gain
6SN7	310	10,000	7,400	8,900	20	4.2
6J6	200	15,000	6,900	11,900	38	9.9
6SC7	780	100,000	50,000	71,000	70	18.7

Type	Theoretical gain	Gain using (7) and values of r_p listed in handbooks	Graphical solution	Experimental gain
6SN7	4.2	4.3	4.2	4.9
6J6	9.9	11.6	9.1	7.5
6SC7	18.7	19.8	17.7	18.5

The graphical solution is provided as a more convenient method of gain determination. It may also be used to study the operating conditions of the amplifier and to determine the presence of distortion in the output.

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NOTES

Note on a Protective Grease for Threads Exposed Under Corrosive Conditions¹

In some problems connected with tropicalization of motor vehicles it became necessary to devise a method of protecting the threads of nuts and bolts to allow for easy removal.

A steel plate, $\frac{1}{4}$ in. thick, was drilled and tapped to take $\frac{1}{2}$ in. bolts. The threads of the bolts and nuts were treated with the following:

1. Light machine oil
2. SAE 110 oil – Hypoid XP lubricant
3. A commercial protective coating grease containing zinc chromate
4. Aluminum stearate grease – commercial
5. Inhibited aluminum stearate grease

The inhibited aluminum stearate grease had the following composition:

2% zinc chromate (as used in paint formulation)

5% graphite (fine flake)

7% aluminum stearate

0.02% stearic acid

Remainder – acid and clay treated Columbia Distillate having a viscosity of approximately 90 S.U.S. at 210° F.

The graphite and zinc chromate were slurried with some of the oil and passed twice through a colloid mill or other shearing device to disperse them. The remainder of the oil and the other ingredients were then added and, after mixing in the cold, the dispersion was heated to 160° C. with constant stirring. This was then allowed to cool and let stand for a period of 24 hr. before using.

The assembly was then tested as follows. The plate with the bolts and nuts was immersed in sea water for eight hours a day, and then put in a heat insulated jar containing water with the temperature at 50° C. After one hour in this cabinet, the heat was cut off and the atmosphere allowed to cool and condense slowly. This cycle was repeated every 24 hr. This combination of sea water immersion and condensation is one of the most severe tests this laboratory has used.

After 10 weeks under these conditions the assembly was tested for ease of removal of bolts. The bolts treated with machine oil only were seized completely. It was just possible to turn the bolts treated with the hypoid lubricant. The ones treated with the two commercial greases could be turned with not too great difficulty. The ones treated with the special inhibited grease could be loosened by hand, and were by far the most easily turned.

¹ Issued as N.R.C No. 1789.

This grease has been tested with bolts and nuts holding together combinations of metals and has also been made up in small batches and used under some rather bad corrosive conditions. In all cases its performance has been satisfactory.

RECEIVED MARCH 29, 1948.
NATIONAL RESEARCH LABORATORIES,
DIVISION OF CHEMISTRY,
OTTAWA, CANADA.

M. COHEN
A. C. HALFERDAHL
I. E. PUDDINGTON

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CANADIAN ERUCIC ACID OILS

I. REFINING AND BLEACHING¹

BY N. H. GRACE²

Abstract

Dark colored commercial erucic acid oils from rapeseed, and from mustard seed screenings (*Brassica* species), have been subjected to various refining and bleaching treatments. Superfiltrol bleaching clay was superior to Neutrol clay or an unactivated Manitoba bentonite. Lecithin-free, partially alkali refined, and alkali refined oils were bleached readily by heating for 20 min. at 100° C., as little as 2% clay yielding oils similar in color to commercial table oils. Crude oils could be bleached without preliminary refining treatment if the temperature were raised to 200° C., though some increase in free fatty acid occurred. With Stanolax as a color standard, relative transmissions at a wavelength of 440 m μ were 4.5% for crude rapeseed oil, 5.0% for alkali refined rapeseed oil, and 58, 78, and 91%, respectively, for the alkali refined oil bleached with 1, 2, and 4% Superfiltrol. The behavior of mustard seed oils was closely similar though more bleaching clay was required. For both rape and mustard, spectrophotometric analyses indicated generally similar transmissions for crude, lecithin-free, and partially alkali refined oils in the range from 225 to 500 m μ , while fully alkali refined oils showed reduced transmissions in the triene region (260 to 280 m μ) with slightly increased transmission over the range from 320 to 500 m μ . Bleached oils were characterized by high transmissions in the range above 320 m μ .

Introduction

The erucic acid oils produced in Canada are obtained from rapeseed and from mustard seed varieties (*Brassica* species) screened from the western Canadian wheat crop. The commercially expelled oils are usually very dark in color and generally unattractive in appearance. The undesirable color of rapeseed oil has been attributed to the presence of chlorophyll in the common black Argentine rape grown in Canada where it ripens unevenly. Whatever the cause, improvement in color is a necessary antecedent to any edible use and to most industrial uses.

Although erucic acid oils have been widely used for edible purposes in India and China, their use as food has been relatively inconsequential in North America. Verbal reports had indicated that effective color removal was difficult, alkali refined oils tending to yield green products on hydrogenation. These statements were confirmed by hydrogenation of commercially available refined and bleached rapeseed oil, which developed the reported dis-

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² Biochemist, Oils and Fats Laboratory.

coloration. A study of the recent literature on German wartime technology shows that rapeseed oil was their chief source of edible fat (3). The present world shortage of fats and the possibility of large scale Canadian production of erucic acid oils were among the considerations leading to this study of processing conditions.

Materials and Methods

Crude rape and mustard oils were obtained from a commercial source in Moose Jaw, Saskatchewan; their general characteristics are given in Table I. These were refined and bleached in various ways, and the resulting oils were examined with special reference to color and free fatty acid.

TABLE I
CHARACTERISTICS OF CRUDE ERUCIC ACID OILS

	Rapeseed oil	Oil from mustard seed screenings
Refractive index, 25° C.	1.4715	1.4735
Saponification value	179	188
Free fatty acid content (as oleic), %	0.4	0.5
Iodine value	103	118
Color		
F.A.C. Standard Colors, not darker than number	21	27
Relative transmission with Stanolax as standard in Evelyn photoelectric colorimeter, % transmission at		
440 m μ	4.5	4.8
660 m μ	32.5	15.0

Conventional alkali refining was conducted in accordance with A.O.C.S. procedures set down for the refining of soybean oils (1). Partial alkali refining involved a similar procedure with the use of an amount of 6% sodium hydroxide solution stoichiometrically equivalent to the free fatty acid content; these oils are hereafter referred to as 'alkali treated'.

A number of rapeseed oil samples were processed as follows: alkali refined by conventional methods; subjected to five water washings at 100° C. to remove lecithin in accordance with reported German procedure (3); alkali treated to yield an oil of about the same free fatty acid content as the lecithin-free sample; and subjected to steam distillation for one hour at 200° C. The mustard seed oil was subjected to alkali treatment and to conventional alkali refining.

The bleaching clays used were two activated, commercial preparations, Superfiltrol and Neutrol (from the Filtrol Corporation, Los Angeles, Calif.), and a Pembina Manitoba bentonite, which was unactivated. The moisture contents of these clays varied from 3.1 to 4.2%. A few trials made use of the American Oil Chemists Society's official Fuller's earth.

The bleaching operation was conducted in equipment comprised of three heating mantles furnished with 500 ml. three-necked flasks. Each experiment was made on 100 gm. of oil. Bleaching clay was added to the cold oil and the free space of the flask flushed with carbon dioxide throughout the heating period. Heating of the mantles was controlled by means of variable transformers set to bring the temperature to the desired point in approximately 10 min., and manually controlled thereafter. Stated temperatures were maintained within $\pm 3^{\circ}\text{C}$. When the desired heating period had elapsed, the mantle was lowered, stirring stopped, and the oil filtered rapidly by suction through a Büchner funnel. Oil samples were stored under an atmosphere of carbon dioxide in ordinary glass bottles in the diffuse light of the laboratory.

Spectrophotometric absorption curves were made on both crude and refined oils with the Model D-11 Beckman instrument, 1 gm. of oil being made up to a volume of 500 ml. with normal heptane and an aliquot taken for measurement in a 1 cm. quartz cuvette. The color of crude, refined, and variously bleached oils was compared by means of the Evelyn photoelectric colorimeter, with Stanolax, a white mineral oil, as the reference medium. Relative transmissions were determined at wave lengths of 440 and 660 $\text{m}\mu$, respectively. These wave lengths were selected because it has been shown that chlorophylls A and B show absorption maxima in these regions (2). The free fatty acid content of oil samples was determined and expressed as per cent oleic acid.

Results

Spectrophotometric analyses of rape and mustard oils confirmed their general similarity. The curves *A* to *D* of Fig. 1 describe the changes in extinction coefficients over the range from 225 to 500 $\text{m}\mu$, for crude, alkali treated, alkali refined, and alkali refined and bleached mustard oils. The alkali refined oil (*C*), compared with the crude oil (*A*), showed higher extinction values in the triene region (260 to 280 $\text{m}\mu$), but above 310 $\text{m}\mu$ the values fell below those for the crude oil. Extinction coefficients for alkali treated oil (*B*) coincided with those for the crude oil (*A*) until the wave length reached 300 $\text{m}\mu$, and thereafter the points fell approximately between those of Curves *A* and *C*. Alkali refined oil bleached with 4% Superfiltrol clay (*D*), in comparison with the unbleached oil (*C*), showed slightly decreased extinction coefficients at 230 to 240 $\text{m}\mu$ but increased extinction coefficients at 260 to 280 $\text{m}\mu$; otherwise the values were virtually identical to a wave length of 320 $\text{m}\mu$. From this point the coefficients fell to an extremely low value, indicating inappreciable absorption beyond 350 $\text{m}\mu$.

Closely similar results were obtained from the spectrophotometric examination of rapeseed oil. The crude, the lecithin-free, and the alkali treated oils gave extinction coefficients that differed slightly over the entire range. The alkali refined oil showed enhanced extinction values in the triene region but lower values above 330 $\text{m}\mu$. Bleached rape oil followed the pattern already described for bleached mustard oil.

Bleaching Clays

It is apparent from the data of Tables II, III, and IV, that Superfiltrol is a better bleaching agent than Neutrol, and very much better than unactivated Pembina Manitoba bentonite. The three clays showed different bleaching

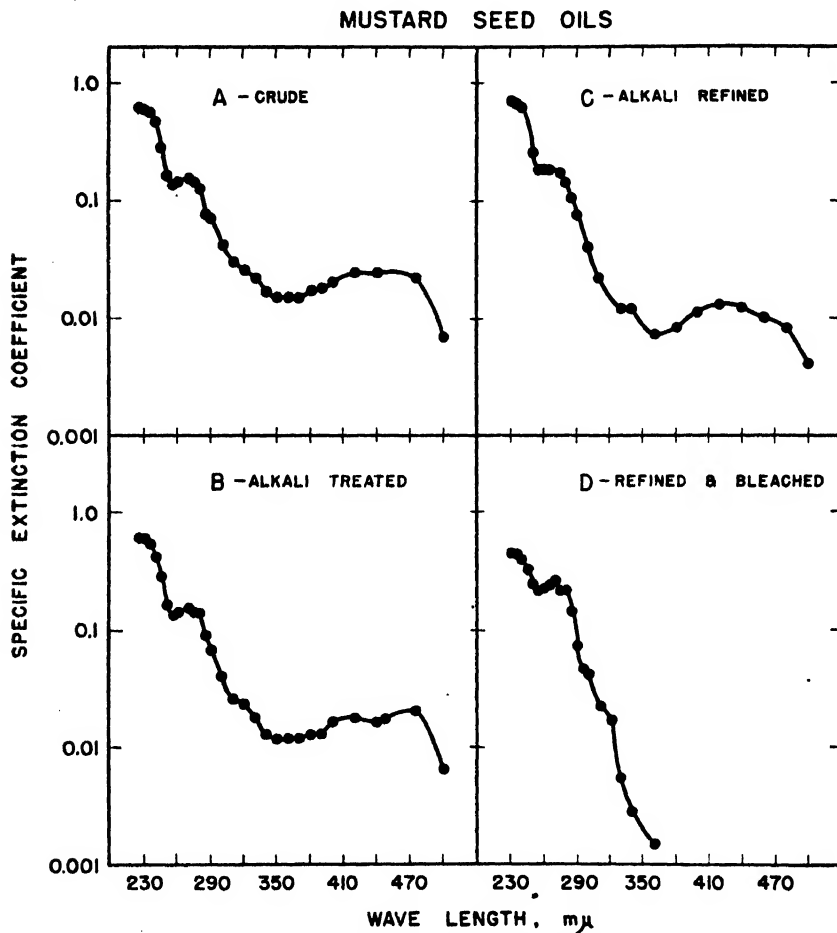


FIG. 1. Ultraviolet absorption curves for normal heptane solutions of variously refined mustard seed oils.

properties when judged by transmission at 660 mμ and the differences were accentuated with transmission at 440 mμ. Also, Superfiltrol did not appear to increase the free acid content when used at 4% for a heating period of 20 min. at 100° C. Superfiltrol was therefore used throughout the remainder of the study.

Effects of Bleaching Conditions

The results of Table V (A) indicate that increase in the duration of heating from 20 to 80 min. at 100° C. with 4% Superfiltrol had little effect on the relative transmission of the oil. There was some indication that the free

TABLE II

EFFECT OF DIFFERENT CLAYS ON THE BLEACHING OF RAPESEED OIL
(Oil heated for 20 min. at 100° C. with 4% of clay)

Clay	Crude oil			Alkali treated oil			Lecithin-free oil		
	F.F.A., %	Rel. transmission		F.F.A., %	Rel. transmission		F.F.A., %	Rel. transmission	
		660 mμ	440 mμ		660 mμ	440 mμ		660 mμ	440 mμ
None	0.42	32.5	4.5	0.24	39.5	4.6	0.29	32.5	4.9
Pembina bentonite	0.58	59.0	4.5	0.33	88.2	18.1	0.23	90.5	13.5
Neutrol	0.40	85.8	9.8	0.32	95.0	47.3	0.20	95.2	34.1
Superfiltrol	0.38	89.0	16.3	0.24	94.9	54.4	0.23	96.1	60.0

TABLE III

EFFECT OF DIFFERENT CLAYS ON THE BLEACHING OF OIL FROM MUSTARD SCREENINGS
(Oil heated for 20 min. at 100° C. with 4% clay)

Clay	Crude oil			Alkali treated oil		
	F.F.A., %	Rel. transmission		F.F.A., %	Rel. transmission	
		660 mμ	440 mμ		660 mμ	440 mμ
None*	0.49	15.0	4.8	0.25	18.1	4.0
Pembina bentonite	0.52	27.9	5.0	0.31	73.8	5.3
Neutrol	0.50	61.0	5.0	0.19	82.9	15.0
Superfiltrol	0.50	80.5	6.0	0.36	91.7	20.5

* The corresponding oil without any bleach.

fatty acid content of crude rapeseed oil rose slightly with the longer heating periods, but this was not noted for alkali treated oils.

The results of Tables IV, V (B), and VI indicate very marked temperature effects, especially evident for transmissions at 440 mμ, which appeared to pass through a maximum at about 200° C. This effect was noted in the crude rape, steam treated rape, and mustard oils, but not in the alkali treated materials. The crude rape oil subjected to steam treatment (Table IV) showed little change in transmission below 175° C. This sample of oil (bleached at 175° C.) was the only one in the entire investigation that was difficult to filter.

Free fatty acid content tended to increase appreciably with an increase in bleaching temperatures, the effect being substantially greater with crude than with alkali treated oils.

Effects of Superfiltrol Concentration

The effects of Superfiltrol over a wide range (2 to 12%) on bleaching for a 20 min. period are illustrated by the data in Tables VII to IX. Crude rape

TABLE IV

EFFECTS OF CLAYS AND TEMPERATURES ON THE BLEACHING OF CRUDE RAPESEED OIL SUBJECTED TO STEAM DISTILLATION FOR ONE HOUR

(Clay at 4% concentration with a 20 min. heating period)

Effect of different clays, at 100° C.

Clay	F.F.A., %	Rel. transmission	
		660 m μ	440 m μ
Ne ole*	0.46	14.9	4.0
Pembina bentonite	0.35	27.0	3.8
Neutrol	0.30	40.0	4.0
Superfiltrol	0.29	44.7	4.2

Effect of temperature of bleaching with Superfiltrol

Temp., ° C.	F.F.A., %	Rel. transmission	
		660 m μ	440 m μ
100	0.29	44.7	4.2
125	0.33	55.2	5.0
150	0.28	57.1	6.0
160	0.38	84.0	22.8
175**	0.53	98.5	54.0
175**	0.69	98.5	52.0
200	0.74	100.0	59.5
225	1.11	98.7	49.3

* Steam treated rape oil, no bleach.

** Duplicates done at different times.

oil, bleached at a temperature of 200° C. (Table VII), required at least 4% clay to effect substantial improvement in transmission at 440 m μ . As much as 12% Superfiltrol with crude oil yielded products inferior in color to those obtained with 6% clay on the alkali treated and lecithin-free oils. The crude rape oil showed very marked increase in free fatty acid content with increasing concentrations of bleaching clay. Since all samples of alkali treated, lecithin-free, and fully alkali refined oils showed comparatively little change in free fatty acid, the effect on crude oil may be largely attributed to the high bleaching temperature.

The data for alkali treated mustard oil (Table VIII) indicate poorer bleaching than for comparable rape oil (Table VII), the difference being particularly evident for transmissions at 440 m μ . Alkali refined oils (Table IX) showed substantially better bleaching than alkali treated oils (Tables VII and VIII), the extent of the improvement being greater for rape than for mustard. It is interesting to note that 10% Superfiltrol was required with alkali treated mustard oil to equal the bleaching achieved by 4% clay on alkali refined oil.

TABLE V

THE EFFECT OF TIME OF HEATING AND THE EFFECT OF TEMPERATURE
ON THE BLEACHING OF RAPESEED OIL

Condition	Crude oil			Alkali treated oil		
	F.F.A., %	Rel. transmission		F.F.A., %	Rel. transmission	
		660 m μ	440 m μ		660 m μ	440 m μ
<i>A. Effect of time of heating. (Oil heated at 100° C. with 4% Superfiltrol)</i>						
Time of heating, min.						
20	0.38	89.0	16.3	0.24	94.9	54.4
40	0.56	92.0	8.2	0.18	97.0	66.0
60	0.56	93.0	15.5	0.20	95.0	59.3
80	0.62	93.0	24.8	0.18	100.0	61.0
<i>B. Effect of temperature. (Oil heated for 20 min. with 4% Superfiltrol)</i>						
Temperature, ° C.						
100	0.38	89.0	16.3	0.24	94.9	54.4
125	0.35	94.8	25.8	0.23	98.5	68.0
150	0.47	94.0	33.5	0.28	98.0	62.0
175	0.50	93.2	33.8	0.90	99.0	66.3
200	0.57	99.0	53.5	0.70	99.1	65.0
225	1.07	98.0	47.7	—	—	—
250	1.61	97.2	33.0	—	—	—

TABLE VI

THE EFFECT OF TEMPERATURE ON THE BLEACHING OF MUSTARD SEED OIL
(Oil heated for 20 min., with 4% Superfiltrol clay)

Temperature, ° C.	Crude oil			Alkali treated oil		
	F.F.A., %	Rel. transmission		F.F.A., %	Rel. transmission	
		660 m μ	440 m μ		660 m μ	440 m μ
100	0.50	80.5	6.0	0.36	91.7	20.5
125	0.45	86.1	6.0	0.52	94.9	21.9
150	0.50	86.2	8.6	0.64	94.5	31.9
175	0.58	88.5	10.9	0.79	95.0	36.9
200	0.84	67.8	5.5	0.80	95.9	37.1

It is also evident from Table IX that 4% Superfiltrol was required to bleach mustard oil to the extent achieved by 1% with rape oil.

Results of bleaching with 4% Standard Fuller's earth of the American Oil Chemists' Society are included in Table IX for both the rape and mustard seed oils for purposes of comparison.

TABLE VII

EFFECT OF SUPERFILTROL CONCENTRATION ON THE BLEACHING OF RAPESEED OIL

(Oil heated for 20 min.)

Clay, %	Crude oil (200° C.)			Alkali treated oil (100° C.)			Lecithin-free oil (100° C.)		
	F.F.A., %	Rel. transmission		F.F.A., %	Rel. transmission		F.F.A., %	Rel. transmission	
		660 m μ	440 m μ		660 m μ	440 m μ		660 m μ	440 m μ
1	0.24	35.8	4.8	0.18	89.8	9.4	0.48	88.7	8.3
2	0.29	72.5	7.2	0.20	92.5	31.0	0.42	94.8	29.1
4	0.57	99.0	53.5	0.24	94.9	54.4	0.23	96.1	60.0
6	0.96	100.2	60.1	0.31	98.0	71.0	0.40	98.9	71.9
8	1.11	100.2	68.6	0.25	98.5	78.5	0.43	100.0	79.3
10	1.29	100.2	64.4	0.22	99.2	84.0	0.44	100.0	85.5
12	1.54	99.5	67.0	0.52	98.8	85.6	0.41	100.0	84.0

TABLE VIII

EFFECT OF SUPERFILTROL CONCENTRATION ON THE BLEACHING OF
ALKALI TREATED MUSTARD OIL

(Heated for 20 min. at 100° C.)

Clay concentration, %	F.F.A., %	Relative transmission	
		660 m μ	440 m μ
0*	0.25	18.1	4.0
1	0.33	53.5	5.1
2	0.40	76.1	7.0
4	0.36	91.7	20.5
6	0.32	94.1	34.4
8	0.38	100.0	49.5
10	0.45	97.9	55.9
12	0.55	100.0	60.3

* Alkali treated oil without any bleach.

Effects of Active Carbon, Added Water, and Modifications in Procedure

It is apparent from Table X that active carbon was somewhat more effective when used along with Superfiltrol (Treatments 1 and 2), but reference to Table VII shows that 4% Superfiltrol alone yielded oil with approximately the same transmission.

Treatment 3 used a five minute heating period at 100° C. prior to addition of bleaching clay. The resulting oil had poorer transmission at 440 m μ than oil from ordinary bleaching (Table V). This suggests that readily volatilizable material did not affect the activity of the clay. The addition of 1 and 2% water (Treatments 4 and 5) showed no appreciable effect. Treatments 6 and 7 involved two 2% Superfiltrol bleachings of mustard oils. But results on comparable oils subjected to one 4% bleach (Tables VII and VIII)

indicate that the double procedure was slightly less effective than the simpler, single operation.

TABLE IX

EFFECT OF CONCENTRATION OF SUPERFILTROL ON THE BLEACHING OF FULLY ALKALI REFINED RAPE AND MUSTARD OILS

(Oil at 100° C. for 20 min.)

Superfiltrol concentration, %	Rapeseed oil			Mustard seed oil		
	F.F.A., %	Rel. transmission		F.F.A., %	Rel. transmission	
		660 m μ	440 m μ		660 m μ	440 m μ
0	0.068	72.5	5.0	0.069	52.0	6.0
1	0.066	100.0	57.8	0.053	90.5	9.0
2	0.037	100.0	78.0	0.064	97.0	33.0
4	0.042	100.0	91.0	0.045	100.0	54.5
A.O.C.S.* 4%	0.076	97.0	52.0	0.138	90.0	12.0
6	0.093	100.0	91.8	0.075	96.5	59.0
8	0.101	100.0	92.0	0.103	97.5	62.0
10	0.132	100.0	95.5	0.200	99.9	64.0
12	0.241	100.0	93.5	0.141	98.5	66.5

* American Oil Chemists Society Standard Fuller's earth.

TABLE X

MISCELLANEOUS BLEACHING EXPERIMENTS ON RAPESEED AND MUSTARD SEED OILS

No.	Description of bleaching and oils used	F.F.A., %	Relative transmission	
			660 m μ	440 m μ
1	Alkali treated rapeseed oil bleached for 20 min. at 100° C. with 4% Superfiltrol and 1% Darco carbon.	0.56	93.0	61.5
2	Alkali treated rapeseed oil bleached for 20 min. at 100° C. with 4% Superfiltrol, filtered, and then subjected to a similar treatment with 1% Darco carbon.	0.20	81.0	53.0
3	Crude rapeseed oil heated for 5 min. at 100° C. then 4% Superfiltrol added and held at 100° C. for 20 min.	0.29	90.0	7.5
4	Crude rapeseed oil, 1% water added and then treated as above (3).	0.26	91.5	14.1
5	Crude rapeseed oil, 2% water added and then treated as above (3).	0.25	95.2	8.0
6	Crude mustard oil heated for 20 min. at 100° C. with 2% Superfiltrol added, filtered, and operation repeated with another 2% Superfiltrol.	0.55	67.8	5.5
7	Alkali treated mustard oil, and as in (6).	0.27	85.4	19.8

Effects of Oil Refining

Neither crude mustard nor crude rapeseed oil showed satisfactory bleaching unless high percentages of clay were used in conjunction with temperatures substantially higher than 100° C. (Tables IV, V, VI, VII). Conversely, lecithin-free, alkali treated, or alkali refined oils bleached fairly effectively. However, conventional alkali refining yielded bleached oils with substantially better transmission for a given percentage of bleaching clay (Tables VII and IX).

Changes in Transmission of Bleached Oil on Storage for Eight Weeks

The data of Table XI give the relative transmissions of bleached rape and mustard oils as determined initially and after standing in the diffuse light of the laboratory for an eight week period. Aging tended to improve transmission slightly, lecithin-free rape oil showing somewhat greater change than either alkali treated rape or mustard oils.

TABLE XI

EFFECT OF EXPOSURE TO DIFFUSE LIGHT FOR EIGHT WEEKS ON RELATIVE LIGHT TRANSMISSION OF BLEACHED OILS

(Oils bleached for 20 min. at 100° C.)

Description of oil	Superfiltrol, %	Relative transmission			
		660 m μ		440 m μ	
		Initial	After eight weeks	Initial	After eight weeks
Lecithin-free rape	1	88.7	97.2	8.3	10.5
	2	94.8	100.0	29.1	32.4
	4	96.1	100.0	60.0	64.8
Alkali treated rape	2	92.5	93.0	31.0	34.8
	6	98.0	99.5	71.0	75.5
Alkali treated mustard	2	76.1	80.0	7.0	8.0
	4	91.7	91.5	20.5	22.0
	6	94.1	96.5	34.4	37.0
	10	97.9	99.5	55.9	57.0

Discussion

These results demonstrate that dark, unattractive erucic acid oils from commercial rapeseed or mustard seed screenings are readily amenable to bleaching. As little as 2% Superfiltrol bleaching clay decolorizes alkali refined oils and yields products similar in color to commercial salad oils, such as corn and cottonseed oils. While the most efficient bleaching was done on conventionally alkali refined material, both the lecithin-free and alkali treated oils yielded reasonably satisfactory products. Interest in these alternative refining procedures resulted from a study of German wartime practice (3).

Such modifications in refining may have a bearing on resistance to oxidation and flavor reversion, and may also provide less expensive procedures in the preparation of oils for industrial purposes.

Crude oils could be bleached with fairly good results at temperatures of the order of 200° C. (Table VII) but an appreciable increase in free fatty acid content occurred. German technology indicates that such oils with 2% or less free fatty acid content may be deslimed with spent bleaching clay, hydrogenated, and then alkali refined. Table V shows that fairly good bleaching of crude oil occurred with 4% bleaching clay and temperatures between 175° and 200° C. with only a comparatively slight increase in the free fatty acid content (0.6%). These results suggest the possibility of applying the German practice. It is possible that direct bleaching of these dark oils at a relatively high temperature may be an economic procedure preparatory to the preparation of sulphated, thermally polymerized, or other industrial oils.

Acknowledgment

The author wishes to acknowledge the assistance of Mr. J. B. Palmer, Technical Assistant, who was responsible for the optical measurements throughout this investigation.

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CANADIAN ERUCIC ACID OILS

II. EDIBLE USE OF RAPE AND MUSTARD SEED OILS¹

BY H. J. LIPS², N. H. GRACE² AND ELINOR M. HAMILTON³

Abstract

Canadian grown rape and mustard seed oils were alkali refined with 10° Bé. sodium hydroxide, bleached for 20 min. at 212° F. with 2 or 4% Superfiltrol, and deodorized at 464° F. for one hour. These oils were lighter in color and more viscous than commercial corn oil, had smoke points over 400° F., and were clear at refrigerator temperature (40° F.). Consumer acceptance tests indicated that the erucic acid oils, either fresh or aged for 10 days at 100° F., were generally as acceptable as corn oil when used as salad oils or for the preparation of mayonnaise and pastry. The fresh oils were generally not as satisfactory as corn oil for the preparation of doughnuts, although some of the aged oils gave results comparable with those for aged corn oil.

Introduction

The possibilities of Canadian-grown erucic acid oils as edible fat sources were suggested in an earlier publication (6). Cold pressed rape and mustard oils have relatively mild flavor and odor and have long been used for edible purposes, chiefly in the Orient and some European countries, but the hot pressed or solvent extracted oils have strong odor and flavor and are not palatable in the unprocessed state. Improved materials of the latter type have had little culinary application except in Germany (6), perhaps because of anticipation of difficulties with flavor reversion (3, p. 194).

The chief requirements for a good salad and cooking oil are: attractive color, agreeable "feel" or "texture" to the palate, bland or pleasing flavor, good keeping quality, high smoke point (preferably over 400° F.), and clarity at refrigerator temperature (40° F.). These points are considered in the present paper in regard to hot pressed, fully refined rape and mustard seed oils, as indications of their acceptability for food use.

Materials and Methods

The crude rape and mustard seed oils used in this experiment were described in the first paper of the series (5). They were refined with 10° Bé. alkali, bleached with 2 or 4% Superfiltrol under carbon dioxide for 20 min. at 212° F., and steam deodorized under vacuum at 464° F. for one hour in the laboratory according to accepted processing methods (3). A special refined, 4% bleached rape oil was prepared by the use of water washing techniques, before and after refining, to remove phosphatides. This procedure was described in

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reports on the German fat industry as an effective means of eliminating flavor reversion (6). The resulting oil contained no detectable quantity of phosphorus and hence was termed "lecithin-free." Each test sample of processed erucic acid oil was a composite of either two or three batches individually prepared from the same source material. Commercially processed corn (salad) oil was used as a reference material in all tests, and comparisons were made on fresh oils and oils aged for 10 days at 100° F. None of the oils showed clouding or precipitation when held at 40° F.

Measurements of color (5), fluorescence (7), kinematic viscosity (2, p. 647), peroxide oxygen (4), free fatty acid (9), and smoke point (1) were made at different stages of processing and use.

Mayonnaise, pastry, and doughnuts were prepared according to the recipes given in Table I. Pastry was baked 10 min. at 435° F. and served at room temperature, and doughnuts were fried in the oils at 355° to 365° F. for three minutes and served warm.

TABLE I
RECIPES FOR VEGETABLE OIL PRODUCTS, GIVEN IN GRAMS

Constituent	Product		
	Mayonnaise	Pastry	Doughnuts
Eggs	—	—	96
Egg yolk	18	—	—
Flour	—	112	500
Sugar	2½	—	200
Oil	200	50	—
Shortening	—	—	25
Milk	—	—	244
Water	15	15-20	—
Baking powder	—	—	15
Cinnamon	—	—	½
Mustard	½	—	—
Nutmeg	—	—	½
Paprika	Trace	—	—
Pepper	Trace	—	—
Salt	1	2	4
Vinegar	15	—	—

The oils and prepared products were scored by a 24-member panel (8); zero represented the ideal in the estimation of the scorer, and excess or deficiency of the property under study was rated on an integral scale of + 5 to - 5. A score numerically greater than ± 2.5 units indicated a definitely unacceptable product. The oils and mayonnaises were rated for color, texture, odor, and flavor, but the pastries and doughnuts were rated for odor and flavor only. All organoleptic data were examined statistically by means of analyses of variance.

Results

Physical and chemical measurements for the corn, mustard, and rapeseed oils at various stages of processing and use are given in Table II. Tables III and IV show organoleptic data for the oils and for mayonnaise, pastry, and doughnuts prepared with them.

TABLE II
CHEMICAL AND PHYSICAL MEASUREMENTS ON VEGETABLE OILS AT VARIOUS STAGES OF PROCESSING AND USE

Oil	Condition of oil				
	1 Bleached	2 Bleached and deodorized	3 Bleached, deodorized, and aged	4 As in column 2, fried	5 As in column 3, fried
Measurement					
<i>A. Transmission, %_o, at 440 mμ relative to mineral oil (Stanolax)</i>					
Corn*	—	32	25	28	27
Mustard, 2% bleach	38	58	51	43	43
Mustard, 4% bleach	50	62	54	44	43
Rape, 2% bleach	75	93	84	64	60
Rape, 4% bleach	85	89	87	62	59
Rape, "lecithin-free"	82	87	84	—	57
<i>B. Fluorescence, Coleman photofluorometer units, 1 gm. of oil in 100 ml. xylol, corrected for fluorescence of xylol</i>					
Corn*	—	71	67	50	49
Mustard, 2% bleach	70	58	57	50	49
Mustard, 4% bleach	68	56	57	58	47
Rape, 2% bleach	11	2	6	10	11
Rape, 4% bleach	3	2	2	10	12
Rape, "lecithin-free"	16	12	11	—	17
<i>C. Viscosity, centistokes at 100° F.</i>					
Corn*	—	33.6	33.5	35.7	34.7
Mustard, 2% bleach	41.6	42.3	42.3	44.6	44.9
Mustard, 4% bleach	41.9	42.3	42.5	44.4	44.4
Rape, 2% bleach	46.5	47.4	47.6	48.9	49.5
Rape, 4% bleach	46.7	46.8	46.8	48.3	49.1
Rape, "lecithin-free"	46.8	47.6	47.6	—	49.8
<i>D. Peroxide value, ml. of 0.002 N thiosulphate per gm.</i>					
Corn*	—	0.0	0.0	3.9	4.5
Mustard, 2% bleach	0.0	0.0	0.0	4.9	5.4
Mustard, 4% bleach	0.0	0.0	4.0	4.3	4.6
Rape, 2% bleach	0.0	0.0	2.6	4.5	4.7
Rape, 4% bleach	0.0	0.0	6.0	4.0	4.6
Rape, "lecithin-free"	0.0	0.0	6.2	—	6.1

* The corn oil was used as purchased and received no further processing. Column 2 gives values for the untreated corn oil and Column 3 for the untreated, aged corn oil.

TABLE II—*Concluded*
CHEMICAL AND PHYSICAL MEASUREMENTS ON VEGETABLE OILS AT VARIOUS STAGES OF PROCESSING AND USE—*Concluded*

Oil	Condition of oil				
	1	2	3	4	5
	Bleached	Bleached and deodorized	Bleached, deodorized, and aged	As in column 2, fried	As in column 3, fried
Measurement					
<i>E. Free fatty acid content, as % oleic acid</i>					
Corn*	—	—	—	0.1	0.1
Mustard, 2% bleach	—	—	—	0.1	0.2
Mustard, 4% bleach	—	—	—	0.2	0.2
Rape, 2% bleach	—	—	—	0.1	0.2
Rape, 4% bleach	—	—	—	0.2	0.2
Rape, "lecithin-free"	—	—	—	—	0.2
<i>F. Smoke point, ° F.</i>					
Corn*	—	445	—	—	—
Mustard, 2% bleach	—	405	—	—	—
Mustard, 4% bleach	—	405	—	—	—
Rape, 2% bleach	—	420	—	—	—
Rape, 4% bleach	—	425	—	—	—

* The corn oil was used as purchased and received no further processing. Column 2 gives values for the untreated corn oil and Column 3 for the untreated, aged corn oil.

TABLE III
DIFFERENCES IN ORGANOLEPTIC RATINGS FOR VEGETABLE OILS AND THEIR PRODUCTS

Material	Texture	Color	Odor	Flavor
Oils	○	**	○	**
Mayonnaise	○	**	○	○
Pastry	—	—	○	**
Doughnuts	—	—	**	**

○ Indicates no significant differences found.

** Indicates highly significant differences (1% level); these differences are shown in detail in Table IV.

The three oils exhibited differences in both experimental measurements and organoleptic ratings. The relative light transmission of the oils at 440 m μ increased considerably in the order: corn, mustard, and rape (Table II), and the scoring panel was able to detect significant differences in color of oils and mayonnaises (Table III). Relative transmissions for the oils at 660 m μ were all in the range 97 to 100%, so these are not reported. Although mustard oil appeared to be the most fluorescent in daylight, corn oil had the greatest fluorescence in ultraviolet light (375 m μ) with mustard intermediate, and rape least. "Lecithin-free" rape was more fluorescent in ultraviolet light

TABLE IV

ORGANOLEPTIC RATINGS FOR VEGETABLE OILS AND THEIR PRODUCTS FOR THOSE ATTRIBUTES THAT SHOWED SIGNIFICANT DIFFERENCES

	Oil				Mayonnaise		Pastry		Doughnuts			
	Color		Flavor		Color		Flavor		Odor		Flavor	
	Fresh	Aged	Fresh	Aged	Fresh	Aged	Fresh	Aged	Fresh	Aged	Fresh	Aged
Corn oil	+0.8	+1.0	+0.9	+0.1	+0.3	+0.1	+1.2	+0.3	+0.1	+0.3	+0.1	+0.5
Mustard, 2% bleach	-0.2	+0.1	+0.1	+0.1	-0.6	-0.1	+0.9	+0.7	+0.8	+0.6	+1.4	+1.0
Mustard, 4% bleach	-0.4	-0.1	-0.3	+0.8	-0.1	-0.5	+0.6	+1.4	+1.4	+0.8	+1.5	+0.8
Rape, 2% bleach	-1.6	-1.7	-0.5	0.0	-0.8	-0.6	+1.0	+0.5	+0.4	+0.4	+0.9	+0.4
Rape, 4% bleach	-1.4	-2.0	-0.1	+1.0	-0.6	-0.7	+0.7	+1.1	+0.5	+1.6	+1.0	+2.3
Rape, "lecithin-free"		-1.7		-0.3		-0.9		+1.6		+0.5		+0.6
Necessary difference (5% level)	±0.5		±0.6		±0.4		±0.5		±0.4		±0.5	

than the other rape oils. Corn, mustard, and rape oils showed increasing viscosity in that sequence, but the panel was unable to detect significant differences in texture of oils or mayonnaises. All initial peroxide values were nil; free fatty acid content of oils after use for frying doughnuts was uniformly small; and smoke points were high, with a slight increase from mustard to rape to corn oil. In spite of the apparent similarity in quality, as assessed by these objective methods, the scoring panel was able to detect significant differences in flavor and odor in some of the products (Table III).

The characteristics of the oils were altered by processing, aging, and frying (Table II). Deodorization generally reduced color and fluorescence but increased viscosity slightly; aging intensified color, had little effect on fluorescence, and none on viscosity; frying increased color and viscosity, decreased fluorescence for corn and mustard, and increased fluorescence for rape oil. Peroxide values of aged and fried oils remained quite low; corn and the 2% bleached erucic acid oils showed the least change.

As shown in Table IV, corn oil was considered too dark and rape oil too light, with mustard approaching the ideal. For mayonnaise, color differences were smaller, and only the rape oil products were thought to be deficient in this respect. Flavor scores for the oils deviated significantly from the nil value for fresh corn oil; and for aged, 4% bleached rape and mustard oils. Pastry and doughnut mean scores were all positive, indicating degrees of excess flavor and odor attributable to the oils used. The erucic acid oils were not as satisfactory as corn oil for the preparation of doughnuts, although some of the aged oils gave reasonably satisfactory results.

The relatively poor flavor scores for fresh corn oil and for pastry prepared with it indicated that the natural flavor of the oil was considered too strong by some of the tasters. This flavor was evidently diminished or obscured by aging and baking or frying. The apparent improvement on aging of some of

the other oils used in the preparation of pastry and doughnuts may have been due to partial volatilization or breakdown of products of aging when the oils were subjected to baking or frying conditions (3, p. 290).

When processing steps are considered in conjunction with experimental results for the single samples used here (Tables II and IV), it would appear that increasing the bleach for rape and mustard oils from 2 to 4% was not advantageous. There was no important decrease in color and more peroxide was formed on storage in the 4% bleached oils. The specially treated "lecithin-free" rape oil (4% bleach) did not show any superiority in organoleptic scores as compared to 2% bleached rape, but was generally better than 4% bleached rape.

Erucic acid oils have hitherto been used for industrial purposes in Canada. These preliminary results indicate that they also merit serious consideration as possible sources of edible materials.

Acknowledgments

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THE OXIDATION, IGNITION, AND DETONATION OF FUEL VAPORS AND GASES

VI. THE PREVENTION OF PRE-IGNITION AND DETONATION IN GAS ENGINES¹

BY R. O. KING², W. A. WALLACE³ AND B. MAHAPATRA⁴

Abstract

The experiments described show that town gas containing hydrogen in large concentration can be used as fuel for a carburetor type Otto cycle engine at compression ratios rising to 10 : 1 and in mixtures with air in any proportion, if the accumulation of fluffy carbon in the combustion space be prevented. The carbon is produced mainly by pyrolysis of the lubricating oil. Confirmation of the nuclear theory of ignition, advanced in Part IV to explain the cause of detonation in engines, is thus obtained. Performance data are given for the variation of power and economy with mixture strength and ignition timing at compression ratios of 6, 8, and 10 : 1.

Introduction

It has long been known that the power and efficiency of gas engines have been limited by the necessity of using relatively weak gas-air mixtures and low compression ratios in order to avoid pre-ignition and detonation. Both effects are commonly believed to be due to ignition of the combustible mixture by sudden compression and/or by hot surfaces in the combustion space. Both increase in severity with increase in the proportion of hydrogen in the gas.

The severity of the effects mentioned has been mitigated by reducing the inflammability of the combustible mixture or by cooling the more highly heated surfaces of the combustion space. Thus, Dugald Clerk (1) added cooled exhaust gases to the entering mixture; Bertram Hopkinson (4) provided a water sprinkler system in the combustion space and a modification of the system was used in the Crossley Gas Engine (2, p. 39). The Koerting Gas Engine (German) was fitted with a separate water cooled body in the combustion space (2, p. 95). Recent developments aimed to avoid pre-ignition and detonation are the high compression gas engine and the Dual Fuel engine using gas and injected oil. Both operate at Diesel engine compression ratios. High pressure gas is injected late in the compression stroke in the first mentioned type (Walter (9) and Erren (3)) and ignition is by electric spark. Ignition is by injected oil in the Dual Fuel type as in the compression ignition engine, and mixing of the gas with air does not occur until the inlet valve opens (Jones (5, p. 37)).

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The above mentioned methods of increasing the power and economy of gas engines are based on the theory that pre-ignition and detonation are inherent in the nature of the gas, especially of the hydrogen constituent. It is shown, however, by the experiments described in Part V (8) that the pre-ignition and detonation observed when hydrogen-air mixtures are used in an engine are due to the igniting effect of finely divided carbon derived from pyrolysis of the lubricating oil.

Commercial fuel gases, even if composed mainly of hydrogen and carbon monoxide, usually contain some proportion of hydrocarbon which by pyrolysis at end gas temperatures might yield finely divided carbon in sufficient concentration to cause ignition and consequent detonation (Part IV (7)). The lubricating oil would otherwise be the sole source of carbon, as when using hydrogen.

It became of interest, therefore, to determine if pre-ignition and detonation in engines using fuel gas could be avoided, as in the hydrogen engine, by preventing the accumulation of finely divided carbon in the combustion space. Experiments made accordingly are described in this Part and show that the gas, pre-mixed with air in any proportion, can be used at compression ratios rising to 10 : 1, the limit of the variable compression C.F.R. engine, without pre-ignition or detonation and with a consequent increase in power and economy.

Experimental

The C.F.R. knock testing engine in the Department of Mechanical Engineering, University of Toronto, was used for the experiments with Toronto town gas as the fuel. The special features of the engine are described in Part V (8).

The Fuel Gas

The composition and calorific value of Toronto town gas are checked continuously by the Consumers Gas Company. The composition at the time of the experiments was as below, in percentage volumes.

Hydrogen	49.1	Ethane	2.3
Carbon monoxide	19.1	Nitrogen	7.8
Methane	12.9	Carbon dioxide	3.7
Heavy hydrocarbons	4.3	Oxygen	0.8

The calorific value was 475 B.t.u. per cu. ft. at 60° F. and 30 in. of mercury barometric pressure, when saturated with water vapor. Temperature at time of use was 78.5° F. and pressure 29.9 in. of mercury, the calorific value being then,—

$$475 \times \frac{520}{538.5} \times \frac{29.9}{30} = 459 \text{ B.t.u.}$$

The gas was supplied to the engine by using the device illustrated in Fig. 1, the standard diffuser being removed from the throat of the carburetor venturi.

The C.F.R. carburetor was otherwise intact and a change to liquid fuel could be made when required.

The rate of gas supply to the engine was measured by a new and freshly calibrated No. 1A Sprague meter.

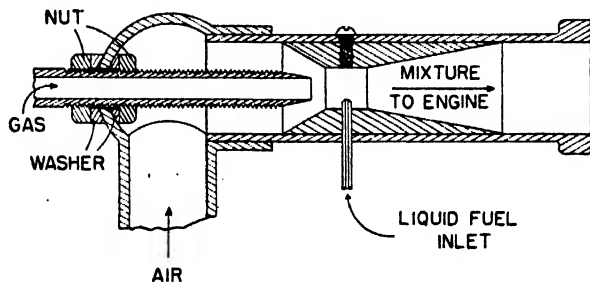


FIG. 1. Carburetor arrangement used for running the C.F.R. engine on town gas.

Experimental Procedure and Conditions

The engine had been run on hydrogen prior to the experiments with town gas and the routine cleaning method then adopted, Part V (8), to prevent the accumulation of fluffy carbon in the combustion space was continued. The engine was always run at 900 r.p.m. The jacket water temperature was maintained at 212° F. by the C.F.R. standard method of evaporative cooling, using distilled water.

The rate of flame propagation in town gas - air mixtures is so much slower than in hydrogen-air mixtures and varies so much with mixture strength that maximum power for a particular compression ratio and mixture strength is obtained only if a particular ignition timing is used. It was decided, therefore, to run series of experiments at compression ratios of 6, 8, and 10 : 1 to determine the ignition timing required for maximum power when using a series of mixture strengths varying from very weak to very rich. Families of graphs were thus obtained relating maximum power to ignition timing and mixture strength at the three values of the compression ratio.

Experimental Results

The combined effect of mixture strength and ignition timing on power output when the compression ratio was 6 : 1 is shown by the graphs of Fig. 2. Similar families of graphs were obtained for compression ratios of 8 and 10 : 1, but are not reproduced.

The graphs of Fig. 3 then give the relation between power output and mixture strength when the optimum ignition timing is used for every experimental point; the timing in degrees advance being given by the figures in circles.

The engine ran smoothly without combustion noise even at the maximum available compression ratio of 10 : 1, and when using the mixture strength and spark advance giving maximum power.

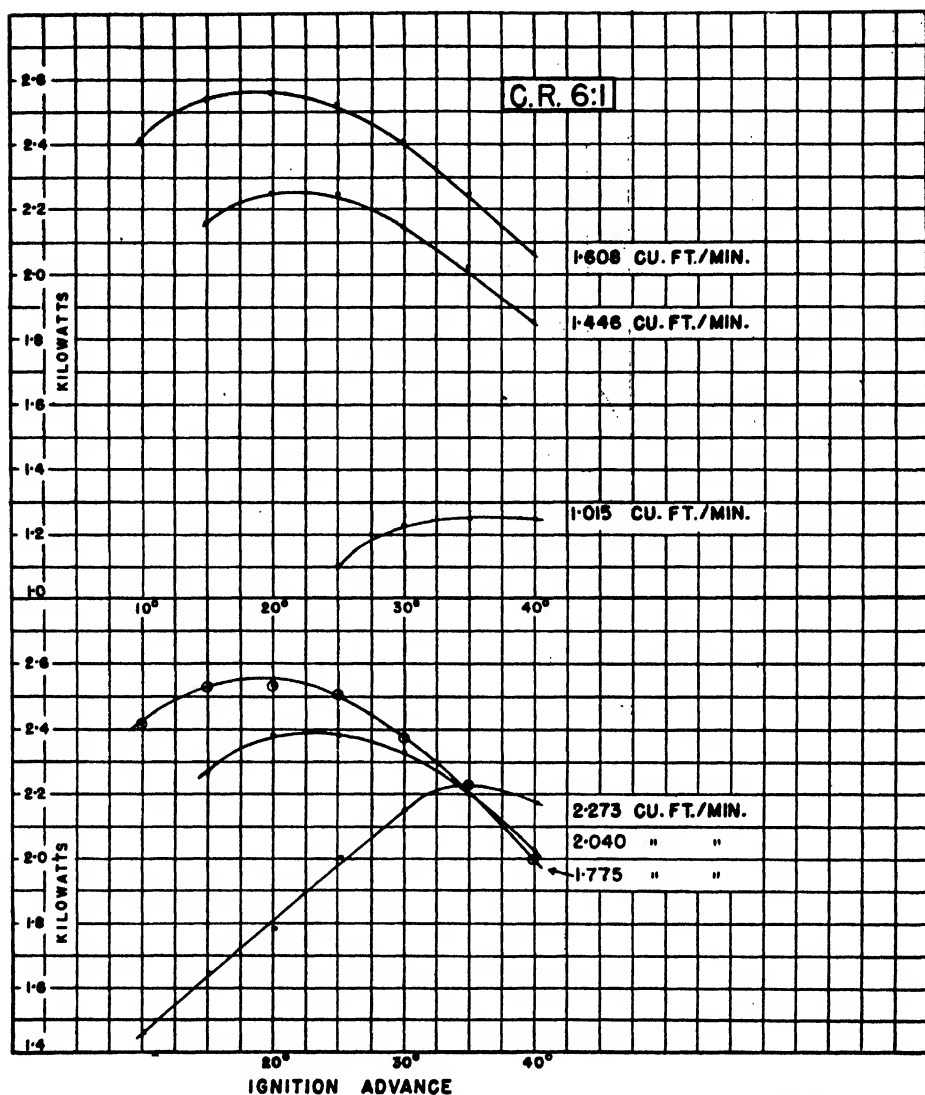


FIG. 2. Effect of mixture strength and ignition advance on power output when using town gas as fuel for the C.F.R. engine, running at 900 r.p.m., compression ratio 6 : 1.

Indicated thermal efficiencies and indicated mean effective pressures calculated from the graphs of Fig. 3 are given in Tables I, II, and III for compression ratios of 6, 8, and 10 : 1, respectively, and for varying mixture strengths. The percentages of mixture strength are in respect of the rate of gas supply required for maximum power, and it will be seen by reference to the graphs of Fig. 3 that this rate varies with compression ratio.

The values for indicated horse power given in the tables were obtained by the usual motor method. The power loss obtained accordingly is added to the net power output. The losses in the C.F.R. unit used for the experiments

are large because they include the electrical and mechanical losses in both the main and auxiliary generators in addition to the pumping and mechanical losses in the engine which could not be measured separately because the engine

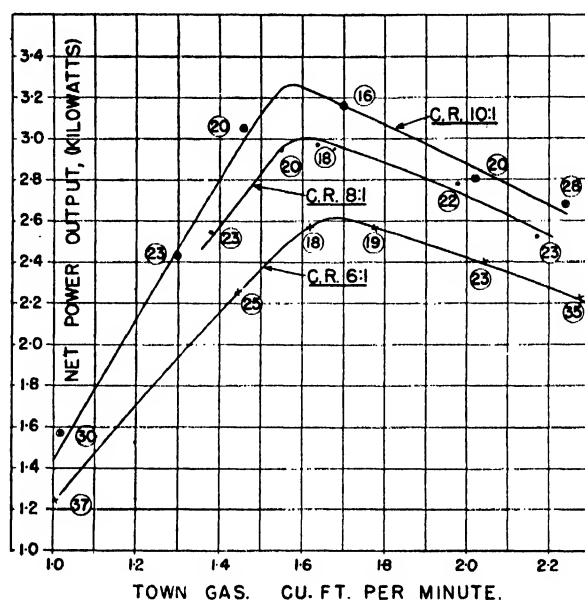


FIG. 3. Relation between power output and mixture strength at compression ratios of 6, 8, and 10 : 1, with optimum ignition advance as shown by figures in circles, C.F.R. engine running on town gas at 900 r.p.m.

TABLE I
COMPRESSION RATIO 6 : 1

Gas - air mixture	Cu. ft. gas/min.	I.H.P.	Indicated thermal efficiency	I.M.E.P., lb./sq. in.
30% weak	1.17	4.20	0.33	98
20% weak	1.34	4.70	0.32½	110
10% weak	1.51	5.19	0.32	121
Max. power	1.68	5.51	0.30	129
10% rich	1.85	5.37	0.28	126
20% rich	2.02	5.24	0.25	122
30% rich	2.18	5.05	0.22	118

was not fitted with a swinging field electrical dynamometer. The total losses measured after the engine had been raised to working temperature by running on benzene were, in kilowatts, 1.61 at 10 : 1 C.R.; 1.59 at 8 : 1 C.R.; 1.48 at 6 : 1 C.R.

The cylinder diameter of the engine is 3.25 in., the stroke is 4.5 in. and as the trials were run at 900 r.p.m., indicated mean effective pressure (I.M.E.P.) in pounds per square inch,

$$= \text{Indicated horsepower} \times 23.41 .$$

TABLE II

COMPRESSION RATIO 8 : 1

Gas - air mixture	Cu. ft. gas/min.	I.H.P.	Indicated thermal efficiency	I.M.E.P., lb./sq. in.
15% weak	1.37	5.48	0.37	128
10% weak	1.50	5.94	0.37	139
Max. power	1.61	6.15	0.36	144
10% rich	1.77	6.02	0.32	141
20% rich	1.93	5.86	0.28	137
30% rich	2.09	5.67	0.25	133

TABLE III

COMPRESSION RATIO 10 : 1

Gas - air mixture	Cu. ft. gas/min.	I.H.P.	Indicated thermal efficiency	I.M.E.P., lb./sq. in.
30% weak	1.10	4.54	0.38	106
20% weak	1.25	5.24	0.39	122
10% weak	1.41	5.95	0.39	139
Max. power	1.57	6.53	0.38	153
10% rich	1.73	6.36	0.34	149
20% rich	1.88	6.18	0.30	145
30% rich	2.04	5.96	0.27	139

Taking the calorific value* of the gas in British thermal units and using f.p.s. units, the indicated thermal efficiency,

$$= \frac{\text{Indicated hp.} \times 33000}{\text{Cu. ft. gas per min.} \times \text{calorific value} \times 778}$$

Discussion of Experimental Results

The primary object of the experiments was to test the validity of the nuclear theory of ignition advanced in Part IV (7) as a working hypothesis for investigations of combustion as it occurs in engines. The results confirm the theory in that ignition of town gas-air mixtures was not obtained by nearly adiabatic compression in a combustion space maintained at 212° F. and containing a hot exhaust valve, compression ratio being 10 : 1, if the concentration of nuclei of ignition, as finely divided carbon, was maintained at a relatively low value.

The experiments considered as engine trials to determine power and efficiency are regarded as of a preliminary nature. Measurements were, however, made with the degree of accuracy usually employed in engine trials and the values obtained for indicated thermal efficiency and indicated mean effective pressure, as given in Tables I, II, and III, are of interest.

* The "higher" calorific value of 459 B.t.u. per cubic foot was used in the calculations.

Indicated Thermal Efficiency

It is generally considered that thermal efficiency increases substantially on going to weak mixtures. This characteristic is shown by the increase of 10% for 6 : 1 compression ratio, Table I, but referring to Tables II and III it will be noted that thermal efficiency tends to become constant on the weak side of maximum power mixture strength, as the compression ratio is increased; furthermore the mixture strength required for maximum power diminishes appreciably as the compression ratio is raised. Both effects may be due to the ignition advance for maximum power at any mixture strength, diminishing as compression ratio is raised as shown by the figures in circles, Fig. 3. Heat of combustion would be added more nearly at constant volume with decrease in ignition advance, and, the combustion period being shortened accordingly, less heat would be lost to the cool surfaces of the combustion chamber. Thus when hydrogen was used in the engine and ignition advance was zero or even -5° , the maximum thermal efficiency obtained, Part V (8), was 0.42 as compared with 0.39 for town gas, or 70% and 65%, respectively, of the air standard efficiency of 0.598 at 10 : 1 compression ratio.

Mean Effective Pressure

A maximum of 153 lb. per sq. in. was obtained for indicated mean effective pressure at 10 : 1 compression ratio (see Table III). The mechanical efficiency of the C.F.R. engine used for the experiments could not be measured but is known to vary from 85% to 88% in engines of the type. Assuming the lower value, 130 lb. per sq. in. is obtained for the brake mean effective pressure. According to Kent (6, p. 1236) it is necessary to limit B.M.E.P. in ordinary gas engines to 65 lb. per sq. in. to avoid pre-ignition and detonation, especially when using coke oven or illuminating gas; both these gases and Toronto town gas contain hydrogen in similar large proportion. The limitation has been shown to be unnecessary if nuclear ignition be avoided, and it is of interest to compare the performance of the C.F.R. engine obtained accordingly with that of the 'National' gas engine in the Heat Engine Laboratory, University of Toronto. The relevant data are given in Table IV.

TABLE IV

FULL POWER PERFORMANCE DATA, C.F.R. AND 'NATIONAL' GAS ENGINES, ON TOWN GAS

Engine	R.p.m.	Gas per I.H.P./hr., cu. ft.	Compression ratio	I.M.E.P., lb./sq. in.	Indicated thermal efficiency
C.F.R.	900	14.4	10 : 1	153	0.38
National	180	18.9	4.85 : 1	95	0.28

The higher mean effective pressure and speed of the C.F.R. have a favorable effect on power-to-weight ratio. Thus, I.H.P. of the C.F.R. is 17.5 per 100 cu. in. of piston displacement, whereas the similar figure for the National engine is 2.17 only.

Conclusion

The experiments show that on preventing nuclear ignition of the gas-air mixture it becomes possible to operate the C.F.R. engine at any desired compression ratio while using mixture strengths varying from very weak to very rich and to obtain corresponding power and economy. The engine was run without throttle control, and, by using a relatively high compression ratio, 10 : 1 for example, power output could be varied over a wide range by controlling the rate of gas supply.

Acknowledgments

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CORROSION OF A STEEL SHIP IN SEA WATER¹

BY K. N. BARNARD²

Abstract

The corrosion of a steel ship in sea water has been investigated by studying the electrical potentials in the sea close to the hull. The surveys were made in conjunction with a drydocking program during which the state of the hull was deliberately altered so that the corrosion patterns could be followed under a variety of hull conditions, and were supplemented by visual inspections of the ship when in drydock. Typical results are described and discussed. Some failures of the present anticorrosive technique are indicated and some possible remedies suggested.

Introduction

Until recent years the corrosion of the underwater hulls of steel ships in sea water was generally accepted to be a necessary evil. The main efforts to mitigate its effects centered around a 'rule of thumb' selection of coatings to protect the major part of the hull, and the use of zinc anodes placed near nonferrous metals to protect the adjacent steel. With the advent of the thin steel hulled minor war vessels up to and including the destroyer class, the corrosion problem became more serious. This stimulated interest in the subject, but attention was given to the development of better types of coatings rather than to the fundamentals of corrosion phenomena.

In general, work on the problem has been confined either to experiments on models or to making visual inspections of ships in drydock. In model research the various causes of corrosion are usually studied separately. No attempts are made to integrate the results experimentally on a small replica of a ship, including its many anomalies. Even if this were attempted, the results extrapolated to full scale could be misleading. For example, little difference in actual size would be expected for an incipient pit whether on a model or on a ship. Yet, because of the vastly different scale, the relative effect of the pit on the model would be exaggerated. If corrosion of a ship is studied by visual inspections alone, a considerable period may be required before changes become apparent, and many of the contributing factors cannot be observed in detail. Hence any comprehensive program aimed at reducing corrosion becomes a very long term project in which a number of ships are treated in different ways and usually examined only at the time of their scheduled refit. Statistical analysis is then applied to the observations, often taken by different personnel.

Naval Research Establishment at Halifax has for some time been carrying out experimental work on hull corrosion, some of which is described in this paper. To gain more direct information, a different method of full scale investigations was adopted, supplemented by visual inspections and model

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experiments. A number of preliminary trials showed that the general corrosion patterns occurring on ships could be satisfactorily located by measuring the electrical potentials found in the sea in the immediate vicinity of the subject vessel. These trials, which were taken on ships at rest, also indicated the desirability of more closely controlled conditions to determine the relative importance of various factors affecting hull corrosion.

In view of this, further trials were carried out over a period of nine months on a steel minesweeper. During this time a drydocking and hull treatment program was followed that allowed the surveys to be made under a variety of hull conditions. Surveys were made after each treatment at frequent intervals, until approximately steady state had been reached.

This report describes the technique and apparatus used; notes some of the advantages and limitations of the method; reviews the causes of cathodic areas; gives a brief history of the ship; outlines the drydocking hull treatment; presents an interpretation of the results of typical surveys, together with a description of pertinent circumstances; and offers a general discussion of the results with a view to possible improvements in the anticorrosion practice for ships.

Surveying Technique and Apparatus

For a steel ship the ohmic resistance of the metallic hull is small compared to that of the sea path and contact resistance between the hull and sea. Thus the potential differences due to the current flow from anodic (corroding) regions of a ship to cathodic regions are greater in the sea than in the metallic circuit.

The potentials in the sea were measured using probe electrodes connected to a distant reference electrode through a millivoltmeter. By surveying over a grid system with the probe electrodes held close to the hull, the approximate positions of the anodic and cathodic regions were determined, and by inference the corroding regions of the hull ascertained.

The search electrodes were made by dipping silver gauze (2 by 6 in.), flame welded without flux to a silver wire, into fused silver chloride which was later reduced to silver - silver chloride by electrolysis. They were mounted concentrically on eight-conductor cable at 4 ft. intervals, one electrode per conductor. Each electrode was lagged with glass wool to reduce water motion at the electrode surface. Phenolite casings were used to protect the electrodes from damage and to allow them to slide easily around the ship's bilge keels. The cable was lead loaded and steel strengthened, and had sufficient negative buoyancy to hang in a vertical plane when held slack. The cable was marked every 4 ft. for 36 ft. on either side of the electrodes to aid in the determination of the athwartship positions of the electrodes.

The reference electrode was also a fused silver - silver chloride electrode. It was connected to a single conductor catbire cable about 350 ft. long. The electrode was held about 60 ft. below the sea surface and was kept away from

the ship by means of floats attached to the cable. The floats usually took the electrode out a distance from 150 to 250 ft., dependent on wind and tide.

To reduce the reading time, a millivoltmeter was used rather than a potentiometer to measure the potential of the search electrodes with respect to the reference electrodes. A suitable switching arrangement connected each of the eight electrodes in turn to the meter. A microammeter (Weston Model 490) with series resistances plus a switch for sensitivity control was used as the millivoltmeter. (The sensitivities were 0.2, 0.5, 1, 2, and 5 mv. per division, the added series resistance being 510, 1,540, 3,260, 6,620, and 16,870 ohms, respectively.) The 1 mv. per division setting was the normal sensitivity used, read to the closest half division. A 200 ft. length of light eight-conductor cable was used as a running lead between instrument station and search electrodes.

The surveys were conducted in Bedford Basin, a region free from industrial disturbances. With H.M.C.S. *Quinte*, which usually was not heavily loaded, it was found preferable to secure the ship by the stern to the buoy. This practice was standard from April 9 on. When the ship was secured by the bow even light winds tended to make it yaw severely, whereas when secured by the stern it kept a very steady position even in heavy winds. To prevent metallic contact between the ship and buoy, rope hawsers were used. The reference electrode was streamed from the bow when the ship was secured at the stern.

The electrode string was hauled taut at each station. The span was 28 ft. To obtain survey readings on a 4 ft. grid, the potentials were measured every 4 ft. along one side, holding say No. 1 search electrode 6 in. below the water line and returning along the other side with No. 8 electrode 6 in. below. This gave some useful overlapping of readings. The athwartship girth of the ship at the station and the distance of the far electrode from the water line were found from the position of the marker nearest the water line. Distances to the stations were measured from the bow. The longitudinal positioning of the electrodes was aided by the presence of vertical rivet lines occurring every 2 ft.

The potential of each search electrode with respect to the reference electrode was measured prior to and after each survey. These zero readings were taken with the electrodes hung from the stern of a wooden harbor craft about 500 ft. from the ship. The electrodes for these readings were kept at an average depth of about 45 ft., to avoid any possible effect caused by the presence of the harbor craft. To minimize extraneous effects, such as air exposure, the electrodes were towed in the water after the initial, and before the final, zero readings. The average value of an electrode's initial and final zero readings was used to correct the survey potential readings of the electrode. The electrodes were left in the sea between successive surveys with all the electrodes shorted, including the reference electrode. The short was removed about two hours before the initial zeros were taken.

When a survey was completed the ship returned to its jetty berth, where it was subjected to continual damage of the paint film at the water line by the jetty fenders. It did, however, make the occasional very short trip to sea.

Plotting

The following method was selected to give a graphical representation of the results of these surveys. The keel line was drawn on cross-section paper and divided into stations corresponding in number to those marked on *Quinte*. At each station a distance corresponding to half the athwartship girth (as obtained during the survey) was marked on either side and at right angles to the keel line. These athwartship marks when joined represented the water line of the underwater girth of the ship measured along the electrode cable position, i.e., the approximate outline of the expanded underwater portion of the hull. The port side of the outline was indicated on the diagram. At each station the athwartship positions of the eight electrodes were marked in with respect to this outline. Points where readings were taken when the electrode cable was moved from stern to bow were marked with a tick (✓) and the appropriate potential marked aft of the tick. A reading taken when the cable was moved from bow to stern was marked forward of a cross (+). The times that the readings were begun and ended on each side were indicated on the figures. The number of days after drydocking may be obtained from the date indicated.

The potential readings were changed to millivolts and corrected for zero out of balance before plotting. In contouring, the interval was not uniform or always the same for each figure, but depended on the general value of the intensities obtained for a given survey. The positive contours were drawn in full lines, negative contours dotted, and the zero contours in broken lines. No allowance was made for the varying distances of the electrodes from the hull, at projecting and re-entrant positions of the hull.

As an aid to the interpretation of results, the approximate positions of the outlets and underwater fittings with respect to the keel line have been drawn on the skeleton expanded diagram shown in Fig. 1.

Advantages and Limitations of Method

Advantages

The advantages of this method of investigation were as follows. (a) The potential surveys were carried out at frequent time intervals, thus following the time changes of corrosion in some detail – without disturbing the process of corrosion. (b) The research was done under practical conditions but avoided frequent (and expensive) drydocking inspections. (c) Information was obtained regarding the relative importance of the various cathodic regions existing on the hull under varied conditions. This information cannot be secured from visual inspection of the ship in drydock. (d) Objective, quantitative results, more impartial than the subjective results of visual inspection, were obtained. (e) Better control was exercised in that, in some instances,

a given factor could be changed as soon as the surveys indicated that its influence had reached an approximately steady state. Thus the time needed for a given treatment was much shorter than would have been the case had drydocking inspection been the only criterion.

Limitations

The surveys were potential, not current density, surveys. Therefore it was not possible to calculate the amount of anodic material entering solution, nor always to rigorously separate anodic from cathodic regions. Consideration had to be given to several factors when interpreting results, particularly when the distance between anode and cathode was relatively short.

The manner in which the potentials were measured should be noted, especially in regard to the zero potential or reference potential. Theoretically the zero potential at a point was taken to be the potential that would be obtained in the absence of the ship. In practice the potentials were taken with reference to that of the sea some distance away from the ship.

The position of the zero equipotential contours for the case of multiple anodes and cathodes distributed at random would depend on the current flow from and to the individual anodes and cathodes. This current flow would be affected by the size, shape, and relative positions of anodes and cathodes, as well as by the presence of polarization and of corrosion deposits. Thus shifts in the zero equipotential positions are to be expected for a ship that had not only multiple anodic sources of the same type (e.g., zinc) but had a steel hull that could be either an anode or a cathode (or both), depending on the condition of its paint and on the activity of its zincs and propellers, all of which were subject to changes in activity, and some in size and position.

Again with multiple anodes and cathodes, two identical anodes, *A* and *B*, might be giving out approximately equal currents, but if *A* were much closer to a cathode than *B*, the potential relatively close to *A* could be much less than that at a similar distance from *B*, owing to the difference in potential gradients. In some cases it was possible for a strong anode (or cathode) to mask the effect of a weak cathode (or anode) close to it. Thus the magnitudes of the potential differences could not be taken as a hard and fast measurement of the relative activity of a given anode or cathode. Their relative positions had also to be taken into consideration.

The electrodes were not point electrodes, but had a cylindrical area approximately 1 in. in diameter and 2 in. long. During the surveys, the electrode string was hauled taut, but, because of the conformation of the ship, the distance of an electrode from the ship was not constant. The closest distance the axis of an electrode could come to the hull was $1\frac{1}{8}$ in. The furthest distance was of the order of 3 ft.—this occurred at the stern of the ship when the string was held taut against the bottom of the 'A' brackets, of the shafts or of the rudder. Also, it was not possible to hold the electrodes against the hull at the bow, and near and between the bilge keels. Thus this type of survey cannot be expected to detect the potential differences set up by the very local

currents that may exist on, say, a rusting steel patch, or at pit holes. In general the size and separation between anode and cathode must be appreciable for detection.

The maximum experimental error in zero corrections was of the order ± 3 mv., the chief cause being the change of electrode potential with temperature. The temperature gradient in the sea water in Bedford Basin, as given by bathythermograph surveys was often 10° to 15° F. for the first 25 ft. of water, during the summer months. In early spring and winter, this gradient was much less and the zero error smaller. Small errors in zero were caused by the variation in distance of the reference electrode from the ship. This distance was usually between 150 and 250 ft., dependent on wind and tide. The error introduced by the use of a millivoltmeter instead of a potentiometer to measure the potentials was less than 1%, the resistance external to the meter being approximately 15 ohms. Chloride ion concentration will affect the electrode potential of the silver-silver chloride, but any differences in concentration at the site of the experiments were not considered very significant.

The error in the relative values of the potential between consecutive readings was much less than ± 3 mv. In fact the agreement between values taken several hours apart was good, provided a large temperature gradient was not present or the ship was not in a state of rapid change such as occurred soon after being undocked.

Cathodic Regions

Although anodic regions on a hull are often "too well" defined by severe pitting and rust deposits, direct information regarding the cathodic regions stimulating this corrosion cannot be obtained from visual inspection in dry-dock. Yet such information is essential to a comprehensive picture of the phenomena of corrosion, and consideration of the relative importance of the causes of the cathodic regions may point to possible remedies.

Since information concerning these regions can be obtained by potential surveys and frequent reference will be made to them, it has been considered advisable to anticipate results somewhat by discussing briefly the following causes which may give rise to cathodic regions:

- (a) The negative pole of a galvanic couple between dissimilar metals.
- (b) The effect of the e.m.f. between bare and painted steel, the latter with rare exceptions being the more cathodic.
- (c) The effect of intermittent wetting of bare steel by sea water, such steel being cathodic to bare steel that has been permanently immersed.
- (d) The effect of differences in oxygen concentration. This, in general, is such that the steel area at which the oxygen concentration is greatest tends to be cathodic.
- (e) The effect of the e.m.f. between bare steel and steel coated with mill-scale, the latter being the more cathodic.

In general, the major galvanic couples on a ship are zinc to bronze, zinc to steel, or steel to bronze, zinc being the most anodic material and bronze the most cathodic. The greatest concentration of bronze occurred at the propellers, and during a survey potential measurements were taken close to them. Many outlet fittings, e.g., valves, were also made of bronze, but were recessed in the hull. The search electrodes did not enter their negative field, so the effects could not be followed. The electrodes could usually enter the negative regions of the zinc-to-steel couple. The potential measurements at the bare areas provided a useful criterion to determine whether or not the ship was rusting. If all bare steel areas were found cathodic it was assumed that the ship was cathodically protected, at the expense of the zincs.

The effect of (b) has been found in a number of these surveys, sometimes to a marked degree. In preliminary surveys on another vessel it was found that the potential reading at a patch anodic when bare changed to cathodic after painting with one coat Anti-Corrosive and one coat Anti-Fouling compositions. The existence of an e.m.f. between bare and painted steel has also been shown on models by the presence of a current flow between bare and painted steel, even when the pieces of steel used were cut from the same sample.

The effect (c) is probably a particular case of effect (d). In model work it was observed that when a dry piece of steel, clean or rusty, was continuously immersed in sea water its potential changed over 200 mv. with time, becoming more anodic. If the wet steel were again exposed to the air for a short time, the potential on reimmersion was less anodic than just prior to exposure, even though the steel had not been allowed to dry. In the ship the effect (c) was observed by holding a wet search electrode casing against a bare patch on the hull just above the water line. Large negative readings were obtained, in some instances greater than 175 mv. (the limit of the measuring instrument) with respect to the distant reference electrode. The search electrode held against the hull just below the water line gave much smaller readings, usually negative. With a wet electrode held just out of the water, and not touching the hull, very small readings were obtained as might be expected owing to an increased resistance path.

The effect (c) can occur only near the water line, and in general the effect (d) would be greatest here owing to the presence of the air-water interface. Thus, in the absence of other stronger cathodes, it is to be expected that a narrow strip along the water line will be cathodic, and hence protected to some degree against rusting. However, a slight change in draft will alter the position of the protected area and the area formerly protected will begin to rust, with the result that this water line region is usually rusty. The cathodic intensity at the water line will be affected by the hull condition and by the amount of intermittent aeration and wetting due to waves (for the latter reason the approximate amplitude of the waves, crest to trough, has been noted for each survey).

Only a small amount of millscale was present on this ship, and none after sandblasting. It is well known that millscale will stimulate the corrosion of exposed steel areas. In model experiments cathodic regions have been shown to be present at areas of steel coated with millscale.

Brief History of H.M.C.S. Quinte Prior to Trials

The trial ship was a Bangor-class minesweeper, H.M.C.S. *Quinte*, built at North Vancouver, B.C. and commissioned on August 30, 1941. Its over-all length was 180 ft., beam 28 ft. and gross tonnage 664. The ship was of steel construction and had two bronze propellers. It arrived at Halifax, N.S. (via the Panama Canal) on November 14, 1941, and was then employed on convoy duty in the North Atlantic. In December 1942 it grounded and sank. Salvage operations were carried out from January to April 1943. While the ship was in drydock from December 12, 1943, to April 17, 1944, the damaged plates were repaired or renewed; the hull hand-cleaned with wire brushes, painted with a coat of Anti-Corrosive (A/C) (iron oxide pigment) and a coat of Anti-Fouling (A/F) compositions, and new zincs fitted. The last drydocking, prior to the present trials, was made July 4-6, 1944, for inspection purposes. The hull also was touched up with A/C and A/F paints. The ship then operated in the Bay of Fundy until the end of July 1945, when it sailed to Halifax and remained at a jetty from August until the trials began in March 1946.

Drydocking Program

This program consisted of a series of five drydockings, during which the hull was treated to provide the desired over-all experimental factors. The sequence of these drydockings was such that the following could be determined: the effects of air exposure alone on a ship that had been long out of refit; the effects of fitting new zincs on such a ship; the behavior of a well painted ship having clean propellers, first without then with zinc anodes fitted; and finally the effect of coating the propellers. In Table I is a tabulated summary of these treatments, which will be more fully discussed later.

Survey of Ship in Initial State

This survey, Fig. 2, was carried out prior to the program of drydockings, on a ship that had been out of drydock for about 20 months, the underwater hull having undergone the normal painting treatment and zinc fitting while in drydock. The ship had spent most of the time berthed at jetties and had only partial service at sea.

For this survey, the over-all potential differences were small. No anodic activity at zinc positions was apparent, although it was subsequently found that about 60% of the original amount of zinc fitted to the ship almost two years before was still present. This inactivity of the zincs was caused by the seepage of sea water breaching the metallic contacts at the interfaces between the zincs, hull, and retaining bolts, and by the formation of a heavy adherent

TABLE I

Drydocking	Period	Weather	Treatment	Subsequent time in sea
First	48 hr.	Fair, temp. 25° to 50° F.	Air dried	15 days
Second	48 hr.	Generally fair, 30° to 50° F.	Air dried, 20 new zinc anodes fitted.	21 days
Third	19 days	Dry majority of days. Cool and clear. Four days steady rain	Hull dry sandblasted, including propellers. Painted 1 coat A/C (Bituminous base); 2 coats A/C (iron oxide pigment); 1 coat A/F.* All zincs removed	11 days
Fourth	7 hr.	48° to 55°. Overcast	22 new zincs fitted	5 months
Fifth	24 hr.	Overcast and cool	Propellers painted, zincs cleaned	

* A/C—*Anti-Corrosive*.

A/F—*Anti-Fouling*.

corrosion film on the zinc surfaces. The observed anodic regions, therefore, must have been due to the solution (i.e., corrosion) of the steel at the exposed areas. Subsequent visual examination of the hull showed that the hull was bare of paint at the regions found to be most anodic. Small localized anodic 'hot-spots' (e.g., the many small pits and corroded rivets) were not picked up individually. This is understandable since the potential difference recorded was the average over the area of a search electrode, which was large when compared with the size of some of the anodic sources, and also because at most positions the distances separating the electrode from this type of anode would be relatively large compared with the anode size.

The small negative readings near the propellers indicated that the current to it was minor and, being much less than in a later case when the ship had been freshly painted and propellers cleaned by light sandblasting, demonstrated the protection given by the 'chalking film' coating the propellers. This coating was observed when the ship was drydocked. The general state of the hull is shown by Figs. 23 and 24. It may be seen that extensive damage has been done by corrosion.

Initial Drydocking, March 20-22, 1946

An inspection of the hull showed that the positions of the larger corroded areas, occurring chiefly where the paint film had been damaged by chafing, agreed well with the anodic regions found in the close-up survey of March 15. Other smaller areas, coated with heavy layers of rust, were found where the ship had been supported by bilge and keel blocks, and apparently left unpainted, at the previous drydocking. The excessive pitting caused by the omission of painting such areas can be seen in Fig. 25. Many rivet heads

were badly rusted and several were leaky. Elsewhere, although the plates had been badly pitted prior to the last painting, the amount of new local pitting on the plates was not excessive, considering the time since the ship was last drydocked. The port 'A' bracket and both propeller shafts were coated with heavy deposits of rust. The starboard 'A' bracket had been renewed during the last refit and was in a better condition. It was covered by an almost intact coating of millscale.

Fouling was not excessive and consisted of weeds and mussels. The weeds were spread over the hull as small tufts which were 1 to 3 in. long. The concentration of the tufts was largest near the keel amidships. The mussels were mostly scattered, but had formed clusters around some of the larger outlets. Both propellers were chalked with a fairly thick adhesive grey-white coating. Although a large percentage of the original mass of zinc was still present, all the zinc anodes looked very inactive and were coated with corrosion products.

Surveys of Ship After Initial Drydocking

The survey, Fig. 3, was begun within three hours of undocking. Comparing Fig. 3 with Fig. 2, it is evident that a very marked change in distribution and intensity of anodic and cathodic regions had taken place. The potentials of the water line section had changed from negative to positive. The propeller shafts and part of the keel had become more anodic. At the stern and near the bow, strong negative readings were obtained. The strong anodic readings occurred where the steel was bare of paint (as shown by heavily coated rust patches on the ship in drydock), whereas the intense cathodic areas occurred where the paint was almost intact, and near the propellers.

The reversal of potential at the water line and the increased strength of anodic and cathodic readings is considered an excellent illustration of the important part played by cathodic polarization in retarding corrosion rates. For Fig. 2 the polarization would have reached a more or less steady state, the ship having been continuously in the water for about two years. Immediately after undocking, the ship would be in a depolarized condition. Because the cathodic area (especially the painted area) was large in comparison with the anodic area (bare steel), cathodic polarization would not immediately reach the state it had prior to air exposure. The measurable differences in potential between anodic (bare) and cathodic (painted) areas were thus much larger than prior to air exposure.

In the absence of polarization, the large painted areas would (after two years water soaking) have relatively low over-all resistance and would therefore be capable of receiving a large current. The effect of other cathodes could be masked by this bare-to-painted-steel current, accounting for the absence of the water line cathodic region. The current flow to the water line cathode might be the same in both cases, but after drydocking it would be a much smaller fraction of the total current. It is also to be expected that polarization of the painted areas would again occur with time. Some evidence

of this may be seen in the decrease of negative values at the overlap readings near the stern, in a time interval of about two hours. A survey showed it had definitely occurred by the end of seven days.

Fig. 4 shows the survey results 15 days after undocking. From this survey it is apparent that the hull tended to return to its rather 'passive' state prior to air exposure, and corrosion to proceed at approximately the steady rate presumably existing prior to air exposure.

The fact that air exposure does depolarize the cathodic regions, stimulating anodic activity on reimmersion of the hull, is of importance for merchant ships which suffer major changes in draft, exposing to the air, and subsequently immersing, large steel surfaces (both painted and bare).

Second Drydocking, April 7-9, 1946

The condition of the hull appeared to be approximately the same as in the last drydocking. Some of the looser rust had fallen away and some of the weeds broken off. Old zincs were removed and weighed. Several precautions were taken when fitting the new zincs. The hull was cleaned to shiny steel at all zinc positions by the use of air-driven brushes and chipping hammers. Zincs were fitted around outlet positions, rather than inset in the openings where reliable metallic contacts are difficult to obtain. Washers were welded to the retaining nuts and wherever possible studs were screwed and then welded to the hull. Although no attempt at a special watertight fitting was made, some ozite (a bituminous substance) was applied to a small area surrounding one of the nuts on each of eight zincs to test it as a watertight seal on the outer surface. The new zincs were weighed before the final fitting.

Surveys of Ship after Second Drydocking

The close-up survey, Fig. 5, was begun within three and a half hours of undocking the ship. The most distinctive feature of this survey was the presence of pronounced anodic peaks at the positions of the new zincs. Otherwise, comparing this survey with that obtained immediately after the ship was subjected to air exposure alone (Fig. 3), it can be seen that the hull had a marked tendency to assume the same distribution of anodic and cathodic areas. Thus there were anodic regions at the water line on both sides amidships, and the previously intense cathodic regions were again strongly cathodic (with the exception of the effects at the extreme stern caused by the presence of the new zincs). The slightly anodic regions near the keel at the earlier date had become slightly cathodic.

Three days after undocking, a change from large positive to large negative potentials had occurred in the midships region near the water line, and strong positive readings were found only in the immediate vicinity of zincs. In addition, the less cathodic regions of Fig. 5 had become more cathodic, while the intense cathodic regions had become less cathodic, especially in the region between the groups of zincs just aft of midships and at the stern, where

small positive readings were obtained. This condition remained approximately constant for the next 14 days. Fig. 6 shows the result of the survey at the end of this time.

This behavior of anodic and cathodic regions is explicable on the hypothesis that the various parts of the ship had a different susceptibility to the formation of resistant films by an electric current. The exact nature of the film does not affect the following argument. Since, as seen in Fig. 5, intense anodic peaks occurred in the vicinity of all the zinc plates, it may be taken for granted that the zinc plates were the chief anodic source of current. Current from these plates would initially flow to areas having the greatest tendency to be cathodic, i.e., areas that were cathodic under similar main hull treatment of exposure to air. Immediately after undocking, these cathodic areas, having been depolarized by exposure, had low enough resistance to absorb the current given by the zincs, and in addition to take some current from the bare steel itself. The bare steel areas would not, however, emit as much current as formerly (e.g., Fig. 3) on account of the opposing potential of the zincs with respect to these steel anodic areas. With the current flow a resistant film built up over the original cathodic areas, thus decreasing the current to them. This in turn allowed the zincs to counteract more effectively the current from the anodic steel areas and, in time, to reverse the current flow so that areas formerly anodic became strongly cathodic, e.g., amidships (Figs. 5 and 6). They became, in fact, more cathodic than the painted areas. This was probably due to the absence of the potential drop which was present at the paint barriers. The maximum time required for this transformation was less than three days—the same order of time in which polarization changes occurred after the initial air exposure.

It is of interest that the anodic region between the zincs at the stern and those nearer amidships began to develop within three days of undocking. An experiment was carried out on the seventeenth day to determine whether this anodic region was due to (a) the corrosion of steel in this vicinity, or (b) formation of a resistant film by the zinc-to-hull current, which, altering the potential distribution, shifted the zero potential surface so close to the cathode that the search electrodes were unable to enter its negative region. A current was passed from the hull to an external cathode, and a survey made immediately after the current was broken. The cathode used was a copper plate (16 ft. by 1½ ft. by 1/64 in.), one side insulated with ozite. It was rigged closely under the hull, ozite side out. The hull was connected to the positive terminal of a 4 v. storage battery. The passage of a 30 amp. current for 1½ hr. resulted (Fig. 7) in a reversal of polarity of the region in question (near the stern tubes), giving a potential distribution somewhat similar to that obtained there immediately after undocking (Fig. 5). This reversal of polarity indicates that process (b), the development of the resistant film, was the chief cause of the change in the potential in this region. It is to be noted that the effects on the hull of the passage of current diminished rapidly.

This is seen in the difference in values at the overlap of potential readings (Fig. 7) near the stern, taken approximately an hour apart.

During the survey (Fig. 5) potential readings were also taken with the electrode string slacked off in the region near the propellers so that the distance from the propeller blade to the nearest electrode was approximately a foot, and the distance from a zinc to the closest electrode was at least six feet. The readings obtained with the string held in this position were all strongly positive, indicating that the current to the chalked propellers was relatively small.

Third Drydocking, April 30 to May 18, 1946

The hull seemed in essentially the same condition as at the time of the last inspection. The new zincs showed signs of active attack and corrosion products had adhered to their surfaces. They were removed, cleaned of corrosion products, and weighed. The hull was sand blasted from the keel to the 8 ft. 6 in. draft mark at the bow, to the 9 ft. 6 in. mark at the stern, and to the bottom of the top rubbing streak amidships. The propellers were also cleaned by sandblasting. To avoid rusting due to atmospheric conditions, no sandblasted area was left unpainted overnight. During wet weather the ship was left untouched except for minor places such as the eddy plates, keel, and bilge block positions, which were protected from the rain and could be painted immediately after cleaning. The hull was painted with one coat of bituminous paint, two coats of iron oxide pigmented A/C paint, and one coat of A/F paint. The bottoms of the numerous pits present in the steel were difficult to fill with bituminous paint, the thickness of which also handicapped an even application. This difficulty was overcome by applying the paint with an improvised spray gun working on the aspirator principle, held two feet from the hull, instead of by brush. After the application of the A/C paints, the ship was undocked and moved forward on its keel blocks to permit cleaning and painting of the areas on which the ship had rested. One and a half hours was required to apply the A/F paint, and the ship was undocked two hours after the painting was finished.

Survey of Ship after Third Drydocking

Within four hours of undocking, the hull was, in general, only slightly anodic, Fig. 8, but anodic peaks occurred at some outlets, at the asdic dome and at the broken bilge keel on the starboard side, i.e., at all the places where the paint film was applied to poorly prepared surfaces. (The nature of these places did not permit cleaning by sandblasting or by air driven wire brushes.) A fairly strong cathodic region occurred at the stern. The positions of the peaks indicated that the current flow was essentially from the vicinity of the outlets, etc., to the propellers, and the strength and polarity of the peaks indicated that it was due to exposed steel rather than to the nonferrous fittings.

Three days after undocking, the hull showed increased anodic activity, especially on the port side near the water line. This increase in activity was undoubtedly due to the abrasion of the paint film in this region (the ship having been berthed at its jetty, port side to). Anodic regions at the asdic dome and at the main injection valve were the only indications at outlet positions. The two small anodic peaks present, about 60 ft. from the bow, were probably due to damaged paint at a bilge or keel block. With the increase in anodic intensity, there was a corresponding increase in cathodic intensity at the stern, further evidence that the current was mainly caused by the hull-to-propeller galvanic couple. Nine days after refit, the survey (Fig. 9) showed the state of the ship to be essentially the same, with the addition of an anodic region at the water line on the starboard side. The increase in activity was, undoubtedly, again caused by the abrasion of the paint, the ship having been berthed starboard side to at its jetty.

To show that the anodic regions were points of low resistance, a current (about 30 amp.) was passed to the hull from a copper strip ($1\frac{1}{2}$ by 16 by $1/64$ in.) placed athwartships at the stern. The ends of the copper strip were held 10 ft. below the water level. The hull was then surveyed, Fig. 10, with the current flowing. Strong cathodic peaks occurred at the positions of the previous anodic areas, Fig. 9, showing that such areas were of low resistance. Cathodic peaks also occurred at some of the outlet positions, e.g., main injection. The positive region at the stern was due to the copper strip anode. An important result of this test was evidence that the hull, in a relatively good paint condition, could readily be 'cathodically protected' by means of a current flow of about 30 amp. When the current was broken, the prior disposition of anodic and cathodic regions returned, with some changes in intensity.

The results of the above surveys indicated that the main current was a hull-to-propeller current, and that this current was probably greater in magnitude than it had been when the hull was in a poor paint condition and the propellers chalked. Evidently in the latter case, the coating on the propellers was sufficient to reduce the hull-to-propeller current to a fairly low value even though a much larger bare steel area was available.

Fourth Drydocking, May 29, 1946

Paint was badly stripped on port and starboard sides near the rubbing streaks, owing to damage sustained while the ship was secured to its jetty. Where the paint was missing, rust was present. Rust had also occurred at positions where the ship had sat on the bilge and keel blocks during the last part of the previous drydocking (i.e., after the ship had been moved forward on blocks). These places were shown by the marks of the wood grain in the paint. The rusting had occurred mostly in streaks where the bituminous paint had cracked under pressure. (In general, the potential surveys did not show these places of rusting as strong anodic regions. The only indication of anodic activity was the occurrence along the keel line of slightly greater

than average anodic potentials, showing that if an intense anodic region, not due to a zinc, was detected, the steel must have been entering solution at quite a fast rate from a fairly large area.) The paint apparently had poor adhesive qualities and was brittle. A tap with the end of a wrench caused flakes of paint up to half-inch square in size to come off, revealing a dry, shiny steel hull.

Where paint was undamaged by chafing, etc., it had prevented further action at rivets and old pits. Active pits could readily be detected, but occurred only at a few scattered places.

The condition of the A/F paint was not good. Even though the ship had been put in the water with the A/F paint in a tacky condition, the paint was dry and hard when the ship was hauled out of the water. There were also a number of small circular patches where the paint was missing, especially between the bilge keels. This was caused by the formation of salt droplets on the A/C paint during the previous docking, after the position of the ship in its cradle had been changed. When the ship was hauled out (in the rain) most of the salt water ran off the hull, or was washed off by the rain. However, on the protected areas, e.g., between bilge keels, the sea water ran into droplets and was not washed off. These droplets were dry when the A/F paint was applied, but the crystallized salt deposited by the drops prevented the A/F paint adhering to them. The hull was free from all animal and vegetable life.

All the damaged paint areas were touched up with one coat of A/C and one coat A/F, with the exception of some of the water line areas on the port side amidships and forward.

In fitting new zincs a different method was tried in an attempt to make and maintain a waterproof metallic contact between the hull and the zinc. Securing bolts were used to make the contact. Rubber washers between the zinc and hull, and an ozite coating over contacting nut or bolt heads were used for waterproofing. Steel washers were welded to all retaining nuts, or studs, and the threads were tinned with solder. All zincs were weighed to the nearest ounce and their approximate exposed area determined.

Surveys of Ship after Fourth Drydocking

A survey was made within a day of undocking (Fig. 11). Anodic peaks were present only in the vicinity of the zincs. The main cathodic region occurred at the stern while lesser cathodic regions were found at the asdic dome (not fitted with zincs) and near the water line on the port side. (This side of the ship had been next to the jetty overnight, and the touch-up painting was not completely applied on this area.) The distribution of anodic and cathodic regions indicated a main current flow from zinc to propeller, a minor current from zinc to hull, and no current from hull to propellers.

Not all zincs had noticeable positive peaks. Some peaks were absent at the stern, and those present were small compared with the peaks obtained after the second drydocking (Fig. 5), when the propellers were chalked, and

the zincs put on a hull in poor paint condition. The absence of positive peaks was not considered to be due to a small current flow from the zincs in this region, but rather to the position of the zero equipotential surfaces with respect to these zincs. The main current flow was from the zincs to the propellers. The zincs were in scattered positions over the hull, and the zero equipotential surfaces of the composite battery ran closest to those zincs nearest the cathodes, i.e., those near the propellers, even though the current density at these zincs may have been slightly higher than at those further away. In the case of the second drydocking, however, the main current was from zincs to hull rather than from zincs to propellers, which caused the zero potential surfaces to lie close to the propellers and away from the zincs in this region. This was indicated by the presence of intense cathodic regions on the hull itself, and by their absence near the propellers when search electrodes were held within a foot of them.

Surveys made 4, 9, 12, 19, 28, and 34 days (Fig. 12) after undocking showed the following characteristics: positive peaks only near zincs; an increased spread with time of the positive region at the stern and a corresponding decrease in the negative region near the propellers; a general increase in intensity of the negative potentials on the hull; and a decrease in the negative peak at the asdic dome with time. The increased negative potentials on the hull occurred particularly at the water line, where the paint film was abraded first on the port side and then on the starboard side—the ship was berthed for only a short time starboard side to. On and after the ninth day, the negative pole of the zinc-propeller current was to be found only by lowering the electrode string away from the hull towards the propellers. (The negative readings obtained near the propellers do not appear in the plotted results, which were for the electrodes held as close to the hull as possible.) The spread of the anodic region at the stern was of special interest in that it showed the change that can occur in the position of the zero equipotential surface. As stated in the preceding paragraph, this surface at first ran close to the zincs near the stern. It then moved further away from the stern zincs and nearer to the propellers with increase in 'effective' length of path due to current flow between stern zincs and hull. Thus it could not be said, when discussing Fig. 11, that the stern zincs were producing a relatively small current, nor, from the results shown in Fig. 12, that the propellers were not receiving current. This demonstrates the necessity of exercising care when interpreting the results of this type of survey. On the thirty-fourth day an inspection of the water line showed the visible bare patches of the hull to be bright and free from rust.

Thirty-six days after undocking, Fig. 13, a change in anodic peaks had occurred. Additional anodic peaks had appeared near the water line on the port side in previously cathodic places, while the intensity of the cathodic peaks on the starboard side had increased. Two factors tended to bring this about. (a) The propellers had been recleaned the day before the survey by a diver using an air-driven brush. (b) The ship had been berthed starboard

side to. The net effect was to give the zincs more work by exposure of a larger area of steel and by removal of some of the deposit formed on the propellers during the five weeks since undocking. The presence of an anodic region on an area of steel surface where no zincs were present showed that the zincs under the new load were unable to protect the hull 100% effectively. As there were only two days between this survey and the previous survey, it is probable that the cleaning of the propellers had had the greater effect. The increase in area of exposed steel would only be slight, as the ship had already been subjected to abrasion on that side for a few days. The additional current required to prevent the rusting of the steel could not be supplied by the zincs because of the continued formation of the corrosion product on their surfaces. This product forms a resistant layer which decreases the available current as time goes on.

Considering the results obtained with the new zincs on a poorly painted ship, it was surprising that (non-zinc) anodic regions should appear so soon, when only a relatively small amount of bare steel was exposed to the sea, and especially as the zincs seemed equally active for both cases. This is a further demonstration of the desirability of counteracting the influence of the propellers, since in the case of the poor paint job the chief factor favoring protection was the chalked condition of the propeller.

Why the anodic region caused by the solution of steel should first appear on the port side, while the starboard side remained cathodic, is also a minor question. Possibly the zincs could supply only sufficient current to the propellers and painted areas to maintain their potential equal to that of unpolarized steel. Then local action could occur on the steel, and the cathodic regions on it would be those having greater available supply of oxygen and the greater intermittent water line exposure. The paint on both sides was damaged near the water line, but the damage on the port side was at a slightly greater draft than on the starboard side, as the ship had had a shallower draft when berthed port side to. Another explanation could be the difference in length of the effective current paths in the sea from the zincs to the exposed areas on the two sides.

Surveys made 44, 55 and 65 (Fig. 14) days after undocking showed further increases in anodic regions on both sides of the ship where steel was exposed. Visual inspection showed the bare areas at the water line to be rusting and there was some evidence that the length of the equivalent current path might play a part in determining which bare spot would rust first. The cathodic regions near the propellers showed a small decrease in area and intensity. The development of anodic sources on the steel itself and a decrease in the zinc efficiency changed the relative geometrical positions of sources and sinks, and caused a shift in zero potential away from the propellers. This shift would tend to accentuate the apparent weakening of the zincs at the stern, i.e., some of the zincs might still have been quite active, although their anodic peaks were masked by the nearness of cathodic sinks—the propellers. (From an inspection of the zincs at a later drydocking, it was evident that five of

the zincs at the stern had not remained active very long owing to a failure of hull-to-zinc contact.)

In order to obtain more information on the masking effect, an attempt was made to chalk the propellers by passing a current of about 30 amp. for about 50 hr. from a copper plate placed just below the propellers. The survey results are shown in Fig. 15 (68 days after refit). A marked change from the previous survey (three days earlier) was observed in potential distribution.

The change would have been more striking but for a lapse of time between the stoppage of the current and the survey (approximately 14 hr.). The anodic zones at the stern had reappeared and were still fairly strong about 17 hr. after the passage of current. In an additional two hours, the region in the vicinity of the propellers had begun again to show negative values, hence the effect was not all permanent. Part of the effect was probably due to permanent chalking, the rest to temporary deposition and polarization. Also, some of the zincs may have been reactivated by having their corrosion product loosened, which would allow them to furnish a greater current. During the survey the bare patches at the water line became more positive with time, as shown by the two sets of readings taken on the starboard side just over three hours apart. These readings indicate that, had the survey been conducted sooner, the whole water line would have been fairly strongly negative and the hull cathodically protected. It is thus again apparent that an additional current of approximately 30 amp. gave complete cathodic protection to the hull.

Seventy-five days after undocking, Fig. 16, the ship had reverted to its approximate state prior to the passage of current. If anything, its condition had deteriorated, as shown by a decrease in the anodic peaks at most of the zincs, and a spread of anodic zones near the water line. The zinc anodic peaks at the extreme stern did not decrease in intensity, indicating that the propellers were somewhat chalked by the passage of the current. The cathodic intensity very near the propellers was less than that prior to chalking, but greater than that immediately afterwards.

Seventy-six and seventy-seven days after undocking, 19 of the zincs were cleaned by a diver using a small wire hand-brush; 15 on the first day and 4 on the second day. This cleaning was done to determine which was the more important factor in decreasing the activity of the zincs: (a) the corrosion film formed on the surface of the zincs; or (b) a poor electrical contact between the hull and the zincs. If (b) were the major cause, cleaning the surfaces of the zincs would have little effect, whereas if (a) were the cause, a rejuvenation of the zincs would be expected. (The diver's reports on the comparative depth of pitting on the zinc plates were not very consistent, the general report indicating that the zincs were not very badly pitted, and that the corrosion film on the zincs was thin (about 1/16 in.) and fairly easily removed.)

A survey, Fig. 17, carried out on the second day, showed a definite increase in anodic peaks near the zincs. This indicated that (a) was the more important factor in the decrease in zinc activity. No negative readings were obtained

when the electrodes were lowered into the immediate vicinity of the propellers, although the potential readings were only slightly anodic in this region and the gradient such as to indicate a cathodic sink in this area. A change from anodic to cathodic values occurred in many places over the hull, a noticeable exception being the starboard side water line. Why the starboard should remain rather extensively anodic while the port side became mostly cathodic is unknown, but the occurrence is suggestive of Fig. 12, where the port side became anodic while the starboard side remained cathodic. The explanation may again be that the zincs were just sufficiently active to polarize the propellers and painted areas to the potential of steel, allowing local action on the steel to take place. In this case, after the diver started to clean the zincs, the port side was next to the jetty for about 20 hr., as compared with 2 hours for the starboard side. The most important fact is that with only one major change in the general state, i.e., the removal of the corrosion film on the zincs, the ship, which prior to the change was poorly protected, became almost fully cathodically protected.

Eighty-four days after undocking, a week after the cleaning of the zincs, the anodic regions (Fig. 18) of the steel near the water line had increased in area and intensity, while those caused by the zincs had decreased. The decrease again indicates the undesirable formation of the resistant layer on the zincs and the rapidity with which it will reduce their effectiveness.

Surveys made 99 and 112 days after undocking showed: the development of an anodic region near the bow, the first definite evidence of the failure of the paint film, other than where damaged near the water line; a progressive decrease in zinc anodic activity; a change in depth of anodic peak positions, due to an increase in draft of the ship; and a general decrease in intensity and area of most cathodic regions, except for the beginning of cathodic regions at the water line on the starboard side. The last effect was probably partly caused by the increase in draft, but it indicated that the propellers had become chalked again, and were not stimulating the corrosion of the steel to the same extent as previously. This point was tested by recleaning the propellers on the 113th day and surveying the following day. (The cleaning was done by a diver using a rotary air-driven brush. During the subsequent drydocking the outline of where the diver had cleaned could be seen, and it was estimated that while about 30% of the port propeller had been fairly well cleaned, not more than 5% of the starboard one had been cleaned.) The results of the survey showed an increase in anodic activity and the disappearance of cathodic regions at the water line, i.e., cathodic control of the current to the propellers.

On this day another test was made. Readings were taken both with the propellers stopped and with them rotating at approximately 5, 40, and 60 r.p.m. The electrode string was held slack over the stern so that No. 1 and No. 8 electrodes were $24\frac{1}{2}$ ft. deep in the water. The readings were, in general, about 4 mv. more negative with the propellers turning than when stationary (the average reading with them stopped being about 1 mv.). There was, however, very little difference in readings obtained at the different

speeds. Apparently a very slow rotation was sufficient to make the difference, and increasing the speed had little effect. Once the engines were stopped, the readings returned to their normal value in about five minutes and the process could be repeated by further turning and stopping. Almost immediately after the propellers started turning, the readings increased negatively. Two possible causes were: (a) depolarization effects of moving water on the propellers and the steel, and (b) improvement of contact between propeller shaft and hull by turning. Either of these causes could increase the current between the hull and propellers, and search electrodes placed in the area near and below the propellers would measure the relative increase in negative potential at the negative pole, i.e., at the propellers. Four days later, in an attempt to differentiate between (a) and (b), two phosphor-bronze bars, about 2 in. wide, $\frac{1}{8}$ in. thick and 15 in. long, were used to connect the hull electrically to the section of each shaft carrying the propellers. The contact areas were well cleaned. Potential measurements near the stern were made with the electrodes No. 1 and No. 8 held $24\frac{1}{2}$ ft. deep. No differences in reading were observed whether or not the shorting bars were connected. Thus (a) was the probable explanation. The effect of the turning propellers had decreased from that of the previous survey, the difference being only about $2\frac{1}{2}$ mv. with the electrodes in similar positions. These measurements were carried out five days after cleaning the propellers and indicated that the propellers had become more chalked in this time. On the same day a complete survey of the ship was made with the propellers stationary, followed by a partial survey with the propellers turning at about 40 r.p.m. and a repeat over the same section with the propellers stationary. The agreement between the two sets of readings, taken approximately two hours apart with the propellers stationary, was in general good. The anodic readings obtained with the propellers rotating were usually more positive (order of 6 mv.) than either set, while the cathodic readings generally tended to become more positive (2 mv.) towards the bow and more negative (3 mv.) towards the stern. Two complete surveys were made six days later, one with the propellers turning, the other with them stationary. Agreement with the previous results was obtained, except that the magnitude of the changes was less. These results suggest that for a ship with relatively clean bronze propellers, the corrosive effect on the steel is accelerated when the ship is under way, and only a few revolutions of the propellers per minute are required to produce this acceleration. They also provide another indication that the state of the propellers controls, in general, the current going to the propellers.

In addition, the above surveys showed increased anodic activity of the steel, both at the water line and at the bow, and decreased zinc activity. The presence of a peak near a zinc indicated that the contact between it and the hull was still good. To determine more readily the number of zincs having a good metallic contact, the zincs were recleaned (by a diver using a small wire handbrush) 125 days after undocking, and the ship was surveyed the following day. Increased anodic activity was noted for zincs situated at

positions forward of the shaft entrances, indicating that their contacts were good. The zinc anodic regions at the stern also increased, but because of the structure of the ship, the short distance between zincs, and the presence of the propellers, it was not possible to distinguish the anodic region of each zinc, hence the number of these still making contact was not determined. A marked decrease in anodic activity of the steel also occurred, both at the bow and at the water line, giving another demonstration that cleaning the corrosion film off the zincs increased the cathodic protecting power of the zincs. The zincs were given only a cursory cleaning by the divers. On drydocking a month later it was seen that pits in the plates, in some instances over a quarter of an inch deep, had not been cleaned out. This superficial cleaning explained the rather rapid increase in the steel anodic regions and the decrease in the zinc anodic regions found during the survey made eight days later.

The last survey of this group was made 152 days after undocking, and three days after the ship had been decommissioned. The survey was, thus, for a dead ship having no stray currents from its electrical supplies, no heat, and no discharge of hot water. The result of this survey is shown in Fig. 19. No major changes in the potentials surrounding the ship were found; the only noticeable changes were due to a further decrease in activity of the zincs. This illustrates that the potentials surrounding a ship are chiefly affected by the condition of the external hull and fittings (e.g., the condition of the paint, zincs, and propellers) rather than by the internal condition of the ship.

Fifth Drydocking, October 29-30, 1946

The visual inspection showed the following: (a) That the prime paint coating was completely perished and, when dry, required only a light push with a fingernail to crumble it, revealing bright steel surface below. (b) A rusted water line region, 2 to 3 ft. deep. (c) Many small rusted areas (usually from $\frac{1}{2}$ to 2 sq. in., with some up to 10 sq. in.) whose shape and disposition indicated that they had occurred where the paint had flaked off the hull. These areas were scattered over the whole hull with a somewhat greater concentration at the bow (Fig. 26). They did not occur on rivets, but seemed to favor flat and previously undamaged regions of the plates, i.e., very few occurred at the location of previous pits. The pits below these rusted areas were as much as 1/50 in. deep, with a distinct wall and a very even bottom. (d) The majority of the zincs had been subjected to a fairly severe attack (see Fig. 27). The remainder had been only superficially attacked; the reason for this was the failure of the metal-to-metal contacts. (e) The propellers were coated with a light film, some of which was difficult to remove with an air-driven rotary wire brush. The pattern of the previous cleaning by the diver, resulting in a lighter coating, could be readily followed. (f) While the ship was in drydock, the paint on drying peeled off in many more small areas, especially on the starboard side, which faced the sun. (g) The fouling was relatively light except for a layer of weeds formed on the port side from the water line down to a depth of about 3 ft. This side was away from the jetty and faced south

when the ship was at its berth from the end of June on. Some small shellfish (up to $\frac{1}{4}$ in.) had formed clusters near the bow; otherwise, scattered tufts of weeds were the only fouling present.

During this drydocking, the propellers were cleaned mechanically and two coats of a lacquer paint applied over their surfaces. The zincs were cleaned with a wire hand-brush, and at least one of the bolts, or nuts, on each zinc slab recontacted. A few of the zincs were reweighed, to determine from their weight loss the approximate average current for the previous five month period. The zincs chosen for reweighing were fairly typical examples, rather than the most severely eaten (which would have been difficult to remove and replace without breaking). Some of the zincs for which the contacts had failed were also reweighed, for purposes of comparison.

The condition of the hull was such that it could have been readily cleaned to shiny steel in preparation for the application and testing of a different type of paint, but as the ship had been decommissioned and was to be disposed of, no other expenditure was considered warranted. As part of the disposal program, the asdic dome was removed.

Surveys of Ship after Fifth Drydocking

Four surveys were made following this drydocking. The first survey was completed within $5\frac{1}{2}$ hr. after undocking. The results, Fig. 20, followed the same general pattern as previously obtained when the ship was in a poor paint condition, the zincs active, and the propellers fouled. Intense anodic regions occurred at zinc positions and at the water line where relatively large areas of the hull were bare of paint. A small anodic region occurred at the asdic dome recess, which now had over 100 sq. ft. of steel fairly well exposed. Other regions were strongly cathodic, although less so than those of Fig. 5. Two causes contributed to the decreased strength.

- (a) The paint condition was worse, with many newly exposed steel areas which tended to be actively anodic. Although their anodic effects were masked, they would still decrease the measurable intensity of the surrounding active cathodes (not polarized).
- (b) The surfaces of the zincs were well cleaned, but they were not bright and their exposed areas were less.

When the electrodes were lowered close to the propeller, no sign of a cathodic sink was encountered, i.e., a negligible current was going to the propellers.

A second survey (Fig. 21) carried out two days after undocking, showed a marked change in potential distribution. The anodic intensity at the zincs had decreased and, as was to be expected, this had allowed the anodic intensity at the steel to increase. The largest increase in intensity occurred not at the water line, however, but more or less along the whole starboard side, especially towards the bow. The port side at the bow remained cathodic, and no cathodic tendency was detected at the propellers. Thus, the anodic increase

at the steel was not due to an increased current flow between hull and propellers. The above facts, when taken in conjunction with the visual observations of the greater peeling of paint on the starboard side, further illustrate the importance of the current flow from bare steel areas to painted steel areas. Even though in this case the paint was loosely adherent to the steel, it still caused anodic stimulation, i.e., corrosion of the bare steel. At the time of this survey, the painted areas probably had become polarized to a roughly equilibrium value, a condition which would allow the effects of the smaller anodic areas to show up. The decrease of anodic intensity along the water line indicates that the water line cathodic regions had begun to play a more important part. On the day of the survey a strong wind was blowing, causing fairly high waves to lap along the ship, which would accentuate this effect. It is to be noted that the readings at overlaps were rather erratic. This would be expected for a scattered distribution of relatively small anodes.

Thirteen days after undocking, the changes noted in the second survey were more marked. The anodic intensity at the zincs had decreased. This was especially noticeable at the stern, where only a small anodic zone occurred near the rudder. The water line had also become more cathodic. With the exception of the zinc anodic zones, the port side was cathodic, and the starboard side anodic. A strongly cathodic zone was encountered when the electrodes were lowered near the propellers. This showed that the effectiveness of the coating on the propellers had decreased in a short time (less than 13 days). As the ship had been towed (about 10 miles) only at slow speed since the painting of the propellers, and the paint film would not likely have been damaged by abrasion, it had evidently become waterlogged during this period, allowing relatively free passage of current to the propellers. This early breakdown of the coating may have been due partly to the shortness of the drying period before immersion.

The final survey, Fig. 22, was carried out 43 days after undocking, just after the ship had been winterized. Most of the zincs were found to be relatively inactive, especially those at the stern. Cathodic zones along the water line were quite noticeable, accentuated partly by the strong wave action present on this day, which intermittently wet a fairly large area of bare steel at the water line. The draft of the ship was less than normal, exposing bare steel to wind and water. Cathodic regions were present at the stern (the order of 60 mv. within a foot of the blades) and on the port side near the bow, otherwise the steel anodic regions had spread.

Variation of Hull Potential

The e.m.f. existing between a ship's hull with its composite sources and sinks, and a standard reference electrode (held at least 30 ft. from the hull) has been briefly called the hull potential. This potential depends on the resistance at each anode and cathode as well as on their individual e.m.f.'s with respect to the reference electrode. The resistance at each anode or cathode depends on the exposed area, film resistance, and polarization. Among

these factors the degree of polarization of the cathode is important in determining the value of the potential of the hull with respect to the reference electrode. For instance, an anode may have an area equivalent to, or smaller than, a cathode, yet, because of the increase in resistance caused by polarization, the resultant e.m.f. of the two in metallic contact is not usually the mean of the two individual e.m.f.'s with respect to the reference electrode, but is generally closer to that of the anode alone. This fact is of interest in that it possibly offers a simple test to determine roughly the degree of polarization of the hull. Some such test will be required if cathodic protection is used as a general prevention against the rusting of ships.

To find the relationship between the potential of the hull and the state of the hull, the potential of *Quinte*, with respect to a silver-silver chloride reference electrode, was measured on the majority of days on which surveys were made. The reference electrode was connected to the positive terminal of the voltmeter for all readings, and the ship's deck to the negative terminal. (The connection to the deck was first tested in several positions, without noticeable change in voltmeter readings; thereafter it was made amidships, starboard side, on a convenient lug.) The voltmeter used had a very low resistance per volt (an Avo-meter instrument) and the potentials can be considered only approximate (smaller than would have been the case had a potentiometer been used). They did, however, indicate the general trend of the change in potential with state of hull, as shown in the following examples.

After the third drydocking, when the hull had been freshly painted, the propellers cleaned, and no zincs attached, the potential reading on the first day of immersion was 420 mv., which increased to 500 mv. by the ninth day. That is, on the first day the resistance between reference electrode and propeller was less than that between reference electrode and steel, and the resultant potential was close to that between reference electrode and clean bronze alone, which is about 400 mv. The small value of the potential indicated that the propeller was not polarized to any extent. As exposure of the steel occurred, its resistance (steel to reference electrode) became less, and the resultant potential of the hull changed towards that of the steel. On the ninth day, a further test was made. The hull was connected to the negative terminal and a copper plate in the sea to the positive terminal of a 4 v. battery. A 30 amp. current was passed for an hour and a half. Prior to the passage of current, the hull potential was 500 mv.; on making the current, it jumped to 1040 mv.; an hour and a half later, before breaking the current, it had increased to 1110 mv.; just after breaking the current it was 750 mv.; and about an hour later it had returned to 500 mv. These values show the effect of polarization caused by passage of current.

On the first day of immersion after new zincs had been added to the newly painted hull (the fourth drydocking), the potential of the hull was 750 mv. Compared with the 420 mv. obtained without the zincs, it is obvious that the degree of polarization of the propeller must have been greater in this case. (The ratio of the exposed zinc to propeller area was of the order of 1 : 6.)

With decrease in the activity of the zincs, and increase in exposure of bare steel, the hull potential gradually changed to 550 mv. and for the next four months stayed between 550 and 600 mv., the value depending on the hull treatment during this period—e.g., zincs or propellers recleaned. As shown in the survey, Fig. 11, the hull was cathodically protected when the instrument indicated that the potential of the hull was 750 mv., while rusting occurred at the lower hull potentials.

Zinc as an Anode in Cathodic Protection—Weight Loss Evidence

This section is included because the supplementary evidence (weight loss) given in Table II shows that cold rolled* zinc, normally fitted, is relatively ineffective as an anode for cathodic protection. For instance, the loss of weight of zinc over a period of about two years, prior to the second drydocking, was about 93 lb., the initial exposed surface area of the zinc being about 13 sq. ft., whereas, for a three week period, the loss of weight of zinc was about 16 lb., the initial exposed area being about 18 sq. ft. That is, if the zinc had maintained only the same average loss of weight for the two year period, as it did for the three week period, not 93 lb. but about 400 lb. would have been used for an exposed area of 13 sq. ft. Thus it is apparent that most of the corrosion of zinc must occur at the initial stage. In the usual case there are two reasons for this: (a) poor contact between zinc and hull due to water seepage corroding the zincs at the contacts, and (b) accumulation of corrosion products on the zincs. Direct evidence of (a) is given in the third section of Table II where it can be seen that the weight loss for the zincs that had poor contacts, due to failure of the watertight seal, was much less than for those whose seals remained intact—though the initial contact between the hull and the zincs with poor seals were as good as those attained normally. The accumulation of corrosion products was apparent from the fact that the approximate weights of the dross removed from the zincs that had been on for two years was 14 lb., and for three weeks was 3 lb.

General Discussion

To provide a background for this corrosion research, ships were examined in drydock with regard to the extent and distribution of corrosion damage, and to the normal shipyard treatment. The majority of these ships were Canadian warships, and any reference in the following to anticorrosive treatment is essentially to Canadian practice.

This discussion deals with the results of surveys carried out on a warship when secured to a buoy. If the ship had been underway, the corrosion patterns would have been different, as indicated by the surveys made with the propellers rotating. Also the ship, although in commission until the last six weeks of the program, spent most of the time at a jetty and it is to be expected that under other service conditions the corrosion patterns would again have

* A stock sheet of zinc contained by analysis 0.24% lead, 0.020% iron, 0.13% cadmium.

TABLE II
STATE OF ZINCS AFTER THREE DIFFERENT PERIODS

Zinc positions	Old zincs in service about 2 yr.				Zincs in service April 9-30, 1946				Zincs in service May 29-October 30, 1946			
	Est. original Exposed area, sq. in.	Weight left, oz.	Est. weight loss, oz.	Original Weight, oz.	Exposed area, sq. in.	Weight loss, oz.	Average current density, ma./cm. ²	Original Weight, oz.	Weight loss, oz.	Average current density, ma./cm. ²	Remarks on zinc condition	
Rudder—Sbdl. fwd. edge	117	286	76	179	100	14	1	193	102	1.1	Well eaten	
Port fwd. edge	118	290	113	176	100	10	0.7	91	103	1.1	Well eaten	
Rudder post—Sbdl.		Missing		80	49	3	0.45	41			Well eaten	
Port		Scraps only		91	58	6	0.75	46			Poorly eaten	
Over sbdl. prop.—Inner	90	221	73	203	90	9	0.7	74	211		Poorly eaten	
Outer	90	219	115	91	208	9	1.1	84	214	0.1	Poorly eaten	
Over port prop.—Inner	89	203	94	201	85	13	1.1	79	202	0.3	Poorly eaten	
Outer	85	193	60	210	89	11	0.9	84	220	0.2	Poorly eaten	
Sbdl. 'A' bracket—Top	81	172	65	164	80	13	1.2	73	159		Well eaten	
Bottom	79	168	70	162	76	7	0.65	72	162		Well eaten	
Port 'A' bracket—Top	162	355	114	172	81	6	0.5	73	184		Well eaten	
Bottom				163	78	13	1.2	64	168		Well eaten	
Fwd. mag. flooding—Port	77	92	38	307	223	17	0.55	188	345		Well eaten	
Combination pump—Port	40	51	16	126	93	8	0.6	90	149		Well eaten	
Bottom				125	86	10	0.8	78	144		Well eaten	
Downtown pump—Port—Top		51	35	108	81	9	0.7	74	136	0.7	Well eaten	
Bottom	40	16		118	93	9	0.7	80	131	0.2	Poorly eaten	
Evap. blowdown—Port		Missing		38	30	7	1.6	20	41		Well eaten	
After mag. flooding—Sbdl.	50	63	23	214	144	11	0.55	120	278		Fairly well eaten	
Condenser discharge—Sbdl.	91	126	48	284	174	14	0.5	174	248		Fairly well eaten	
Fire and bilge pump—Sbdl.	40	51	16	244	169	8	0.35	145	291	0.55	Fairly well eaten	
Discharge fire and bilge—Sbdl.	13	15	7	99	55	5	0.65	49	107		Very well eaten	
Sanitary pump—Sbdl.				86	62	6	0.7	100			Well eaten	
Main injection—Sbdl.				546	345	36	0.75	300	610		Well eaten	
Inside eddy plates—On hull	94	174	36	Not fitted				98	193		Not seen	
On plate	76	143	93									
On plate	82	152	50									
On plate	72	137	17									
On hull	94	174	20									
On plate	71	134	48									
On plate	85	139	21									
On plate	55	124	11									
On plate	68	128	21									
Totals	1959	3861	2376	1485	2567	4304	254	2427	5068			

been different. But many of the contributing factors would be common, and since differences would generally be in degree rather than in effect, the results and recommendations could be applied, with discretion, to the different cases, both in regard to naval and merchant shipping.

As indicated by the surveys on *Quinte*, a ship has three main cathodic 'sinks' which promote the corrosion of the bare steel occurring on its hull, unless the exposed steel is protected by a source of greater anodic activity. These cathodic 'sinks' occur at (a) the painted steel areas, (b) the bronze propellers, (c) the water line. Other cathodic sinks, such as the bronze fittings at outlets and areas of steel coated with millscale, were found to be subordinate. The order of importance of (a), (b), and (c) in promoting corrosion depends on the condition of the hull, and is determined by such factors as the activity of the protecting anodes, the degree of polarization, the type and age of paint film, the thickness of various deposits, and the area of exposed steel.

These large scale experiments have shown that an appreciable current may flow from bare to painted steel. An intact paint film, if of sufficiently high resistance, will considerably reduce corrosion by simply imposing an ohmic resistance barrier between anode and cathode. A paint film of low resistance will protect the area over which it is intact, but stimulates corrosion of the uncovered patches. Paints are frequently applied over rusty or poorly prepared surfaces and hence form only a relatively low resistance barrier to the passage of current. In addition, common types of underwater paints even when applied to prepared surfaces have very low specific resistances after a short period of immersion in sea water.

The effects of this current flow may explain the rapid corrosion of rivets noted on many Canadian warships. Rivets that had an intact coating of paint were not rusted (since they would tend to act as cathodes), but rivets that had no paint covering were usually badly rusted, even though the steel plates (painted) in the immediate vicinity were not. As rivets project from the sides of the ship they are very liable to get a thinner coating, when painted by brushing, than are the surrounding flat steel plates and, on account of their projection, the paint is more liable to be worn off before that of the plates. Hence a condition develops that is conducive to a current flow from the rivets to the paint surface, and the rivets tend to corrode rapidly.

It is well known that a current will flow between steel and bronze (propellers) in metallic contact. As indicated by the results of the surveys, the corrosive effects of this current are most detrimental when a ship is just out of drydock, with small unpainted holidays (e.g., at bilge and keel block positions), a generally intact coat of paint, bronze propellers that have been cleaned and no, or poorly fitted, zincs. In this case the current from the hull is confined to the small areas of bare steel and causes excessive pitting at these places (see Fig. 25). Also, all ships under service conditions are subject to damage to the paint near the water line, hence some method to supplement

painting should be used to protect this area from the action of the hull-to-propeller current. The effect of this galvanic couple will be greater for a ship underway than at rest because of depolarization of the bronze by agitation and possible effects from water moving at different speeds over steel. The current to the propellers decreased with increased chalking of them. Hence the effects of this cause of corrosion tend to decrease with time, and would be further diminished if the propellers could be insulated from the hull, coated with an impervious film, or made from (or coated with) a material having a similar potential to that of the hull.

The effect of the water line cathodic region, induced by differential oxygen concentration and intermittent air exposure, assumed a relatively more important role with increase in the area of bare steel on the underwater hull.

Areas of millscale on steel will stimulate the corrosion of the bare steel and, if of sufficient size, may cause considerable pitting. On *Quinte*, with exception of the starboard 'A' bracket, no noticeable amount of millscale was present, and after sandblasting none was present.

One of the most influential factors in preventing excessive corrosion is the effect of cathodic polarization, which reduces the intensity of the corrosion currents. In the survey of *Quinte* following its exposure to air, it was shown that the magnitude of both anodic and cathodic potential differences was much smaller after polarization had been reestablished than when the ship was in the unpolarized state immediately after undocking.

Polarization also reduces the current requirements for 'cathodic protection'. Cathodic protection of ships has been recommended by many, but, up to the present, main reliance has been placed on paint films to protect the hulls against corrosion, and cathodic protection has been applied only in a subordinate manner by the use of small zinc anodes. The zincs are fastened close to the bronze propellers and at outlets that have bronze fittings, in an attempt to supply the bronze with current from the zincs, instead of from the adjacent steel. When securing the zincs to the hull, no provision is made for maintenance of a waterproof metal-to-metal contact and, contrary to good shipbuilding practice, frequently rusted nuts and bolts, or bronze screws, are used in fastening. Consequently in many instances the metallic contact rapidly deteriorates and the protection fails. Moreover it has been shown with *Quinte* that even though a sufficient number of well fitted zincs would cathodically protect a ship, the corrosion products that formed on the zinc surface would reduce the current below the value required for cathodic protection in a relatively short time (the order of a month). Hence for adequate cathodic protection, measures other than the above should be investigated and applied.

Deposition films on the cathodes (e.g., on the propellers) act in a somewhat similar manner to paint films in reducing corrosion in that they impose resistance barriers and reduce the current density required for polarization. Cathodic protection accelerates the deposition of these films.

The poor performance of the proprietary bituminous-based paint used, both on *Quinte* and in the laboratory, indicated that it is unsatisfactory for use as an underwater paint. Although some of the flaking may have resulted from the passage of current applied 68 days after the fourth drydocking, it is considered that failure was due primarily to its brittleness and its property of extremely poor adherence to clean steel. On drying, the paint became even more brittle and lifeless and many flakes were removed from the steel by the wind. The paint clung to rivet heads and flaked from flat surfaces, in contradiction of the normal state in which the common underwater paints tend to leave the rivets first. This is explained by the care that was taken to apply the paint liberally to the rivets whose roughened surfaces allowed the paint a better mechanical grip than did flat plates. Hence the paint on the rivets could withstand slightly more strain than that on the flat surface of the steel.

It is apparent that there are weaknesses in the present anticorrosion technique used on ships which may result in excessive corrosion. The use of zinc anodes for cathodic protection is unsatisfactory, since they do not remain active throughout the time of service between drydockings. Little is done towards eliminating the current to the propellers. The paint film in general use is of low resistance and is often applied over poorly prepared surfaces. Holidays are left in the paints at bilge and keel block positions and, unavoidably, the paint film is damaged when the ship is at berth. Apart from preventing fouling, a paint film can be worse than none, as it may result in excessive pitting of the bare steel at holidays. It should be remarked that Canadian anticorrosive technique is similar to that of Admiralty, with the exception of the different types of paints used. No direct experience has been had here with the plastic paints of Admiralty or of U.S. Navy manufacture, but it is understood that the U.S.N. paints have given very satisfactory service on one of the R.C.N. ships.

The following suggestions are offered for improving anticorrosion technique: (a) more intensive use of cathodic protection; (b) the use of an improved underwater paint; (c) better preparation of surfaces for painting; (d) more careful painting of rivet heads; (e) coating the bronze propellers with an impervious, adherent paint film, or a less cathodic metal, or insulating them from the hull.

Of the above, (a) is considered the most important. Under service conditions, damage to paint films is bound to occur, even though the films were perfect in every respect when applied, and these damaged places need protection if rusting is to be prevented. In practice, the perfect paint film is not attained, nor would it be necessary if cathodic protection were used to a sufficient degree, although, with a better paint film, the average current density required would be lower.

The general properties of the paint should be such that it forms a tough, non-brittle film that adheres well to a prepared steel surface, has a high electrical resistance, and will withstand the stresses caused by the application of the protecting current. Although no paint film can be expected to withstand the severe abrasion at jetties, it should be capable of withstanding light

abrasion. The high electrical resistance is desirable to reduce the passage of current through the paint to a negligible amount. This is a more important requirement if cathodic protection is not used and the painted steel is cathodic to bare steel. Experiments concerning the electrical behavior of paint films have shown that many paints strip under the action of the protecting current. Other such experiments are required to determine the best type of coating to use with cathodic protection. The stripping of the paint films by the protecting current is not of great importance if corrosion alone is the main problem, e.g., for decommissioned ships, but where fouling of the ship is of primary consideration (as for active ships in tropical waters) paint stripping is serious, since present antifouling technique depends on the special properties of certain paints.

A well prepared surface is essential if the paint is to exhibit best its adherent and high-resistance properties. Otherwise, a break in the film may allow water to seep behind the paint. To provide a better surface preparation, a wet sandblasting technique has become standard practice in the U.S. Navy and is also used to some extent by Admiralty, but has not been tried by the Canadian Navy. The careful coating of the rivets and the elimination of current to the propellers are of less consequence when cathodic protection is used.

As improvements in the technique of cathodic protection, the following possibilities present themselves:

- (a) The use of a different metal to replace zinc as a sacrificial anode. Corrosion products either should not form on the surface of the metal, or should be readily removable and have a very low resistance to the passage of current from the anode.
- (b) The use of a larger anode area in conjunction with either (i) depolarizers that will prevent the formation of the corrosion products on the anode surface, or (ii) periodic cleaning of the anode surface to remove the corrosion products.
- (c) The use of an anode energized by an adjustable external source (e.g., battery or low voltage generator). This should give better control in that the average current density could be altered to suit requirements, i.e., with increase in damage to the paint film, the total protective current could be augmented.

Service conditions must be taken into consideration when deciding on the source of current. For instance, where nearby power sources are unavailable, decommissioned ships could be protected more conveniently by suitable sacrificial anodes suspended from the ship. If an increase in current were required, another anode could be readily added. For ships in active service, however, any anode must be rigidly attached to the hull, and addition of anodes would be difficult, except in drydock. But as these ships have electrical power available, system (c) might be used to advantage.

It is evident from the surveys of *Quinte*, that the current from an actively protecting anode spreads over a considerable area and is not confined to the

immediate area around the anode. (This is well shown in Fig. 9.) Thus even though anodes were not placed in the immediate vicinity of the bronze fittings, the steel near such fittings would not rust if the hull had full cathodic protection. The anodes may, therefore, be positioned with regard to ease of fastening, which will permit a better connection, rather than to nearness to the numerous outlets. It is, however, desirable to have more than one anode, since the current density over a large cathode (i.e., the hull) will decrease somewhat with distance from the anode.* But the variation does not warrant the present practice of scattering small anodes over the hull, often where it is difficult to fit them (e.g., recessed or re-entrant places). For many ships, the long, flat surfaces of the bilge keels would provide convenient positions to fit the anodes. The dimensions of the anodes could then conform with the dimensions of the ship (long and narrow) minimizing the variations in distance between anode and cathode, and placing the anode relatively close to regions requiring greater protection, e.g., bare steel areas near the water line. In all cases the anodes should be fitted with permanent waterproof connections.

When cathodic protection is used as a means of rust prevention, the optimum current value will usually increase with time owing to the abrasion of the covering film exposing an increasing amount of steel. Normally the rate of increase will be dissimilar for any two ships, making necessary a criterion of how much current should be applied at a given time. Preliminary experiments indicated the possibilities of a rather simple test as to the efficacy of a given current flow at any time by measuring the potential of the hull with respect to a standard reference electrode, the reference electrode being held at least 30 ft. from the hull. The value of the potential for optimum current flow will depend on the system used for cathodic protection, and needs to be determined by experience.

Conclusions

By investigating the electrical potential differences in the sea in the immediate vicinity of a steel ship, it has been shown that:

- (1) The corrosion history of the steel ship may be followed in reasonable detail by making potential surveys in the sea surrounding the ship.
- (2) The chief cathodic sinks occur at (a) painted steel areas, (b) bronze propellers, (c) water line.
- (3) Cathodic protection of a ship appears practical, particularly where corrosion is the main problem (e.g., reserve ships). A rather low current requirement is indicated, less than 30 amp. for a Bangor Class Minesweeper, or an average of less than 6 ma. per sq. ft.
- (4) The current from an active anode spreads over a considerable area and is not confined to the immediate vicinity of the anode.
- (5) Zinc is not satisfactory as a sacrificial anode for cathodic protection in sea water.

**To be discussed in a later report.*

Acknowledgments

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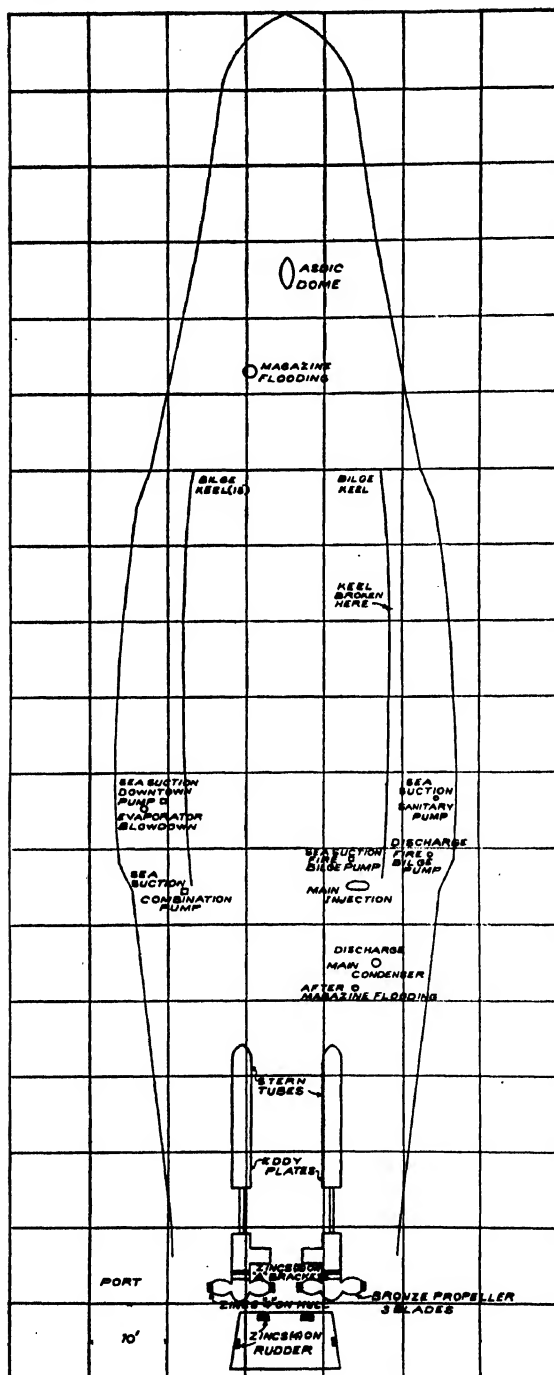


FIG. 1. Expanded outline of the underwater hull, showing relative positions of underwater outlets and fittings.

Outline drawn for ship when drafts were $7\frac{1}{2}$ ft. forward and $9\frac{1}{2}$ ft. aft.

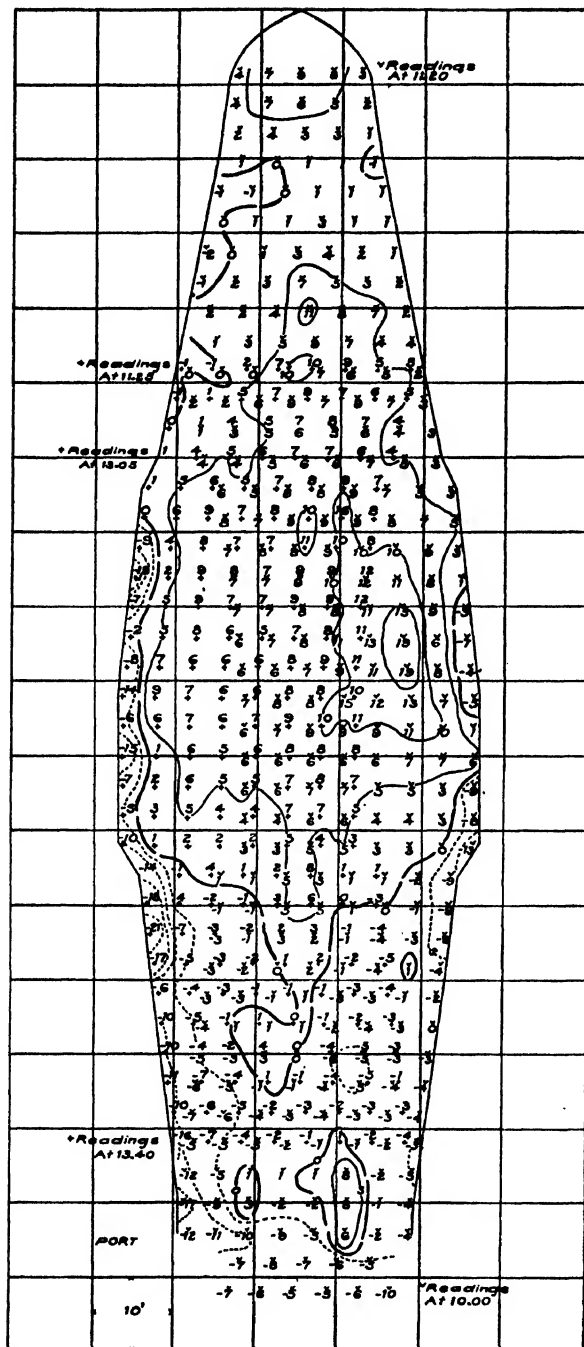


FIG. 2. Results of survey on March 15, 1946.
 Weather—Sunny. Temp. 30° to 47° F. Moderate wind.
 Sea—Choppy.
 Remarks—Ship yawed severely during survey.
 Last drydocking—July 4-6, 1944.

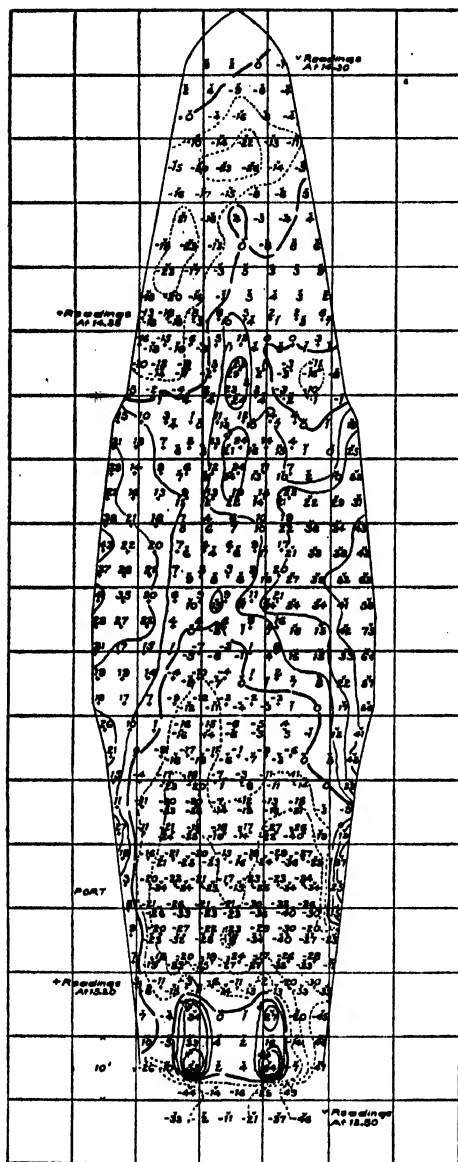


FIG. 3.

FIG. 3. Results of survey on March 22, 1946.
 Weather—Sunny. Temp. 34° to 58° F. Moderate wind.
 Sea—Choppy.
 Remarks—Ship yawed during survey.
 Last drydocking—March 20-22 (1000 hr.), 1946.

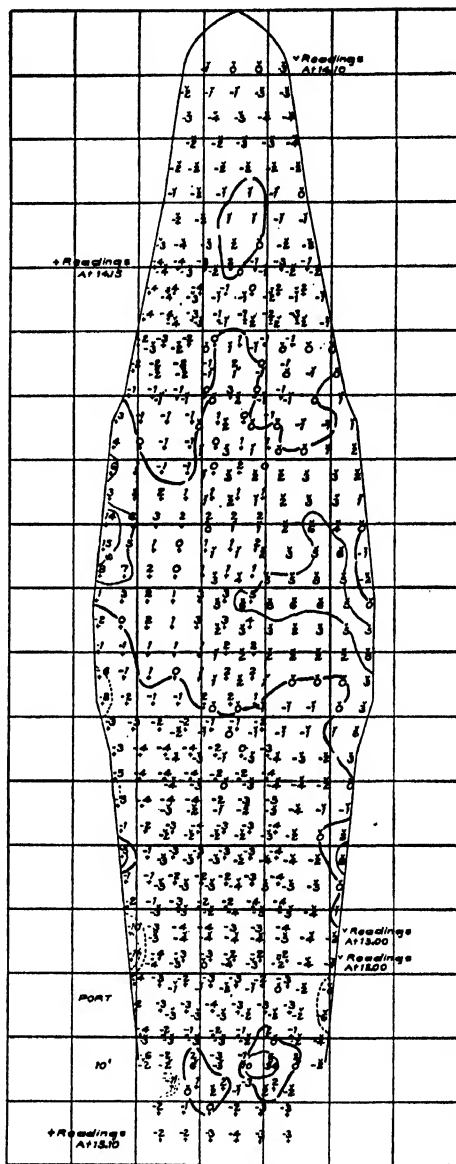


FIG. 4.

FIG. 4. Results of survey on April 6, 1946.
 Weather—Cloudy. Temp. 31° to 37° F. Moderate wind.
 Sea—Choppy, 2 ft. waves.
 Remarks—Ship yawed severely.
 Last drydocking—March 20-22, 1946.

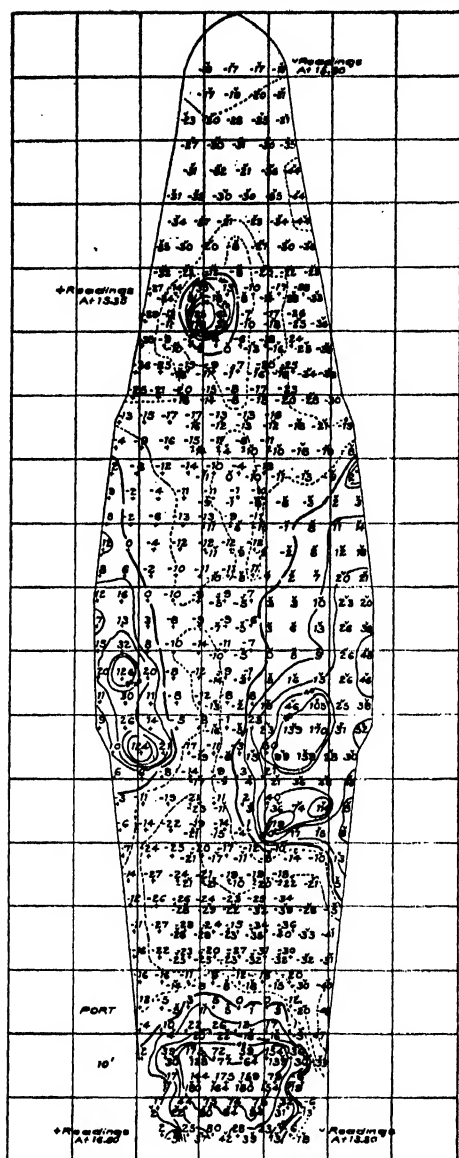


FIG. 5.

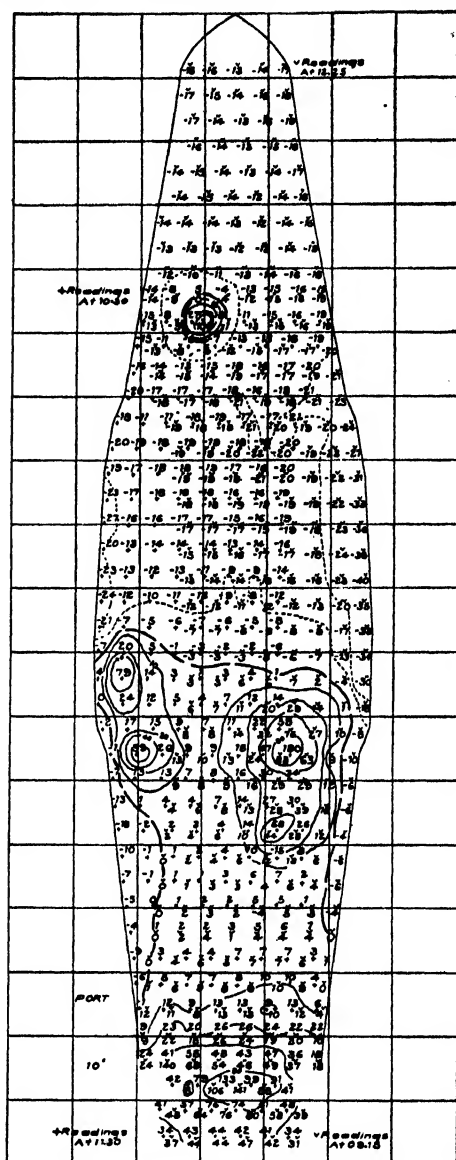


FIG. 6.

FIG. 5. Results of survey on April 9, 1946.

Weather—A.m. clearing, p.m. sunny. Temp. 30° to 39° F. Strong wind.

Sea —1 to 2 ft. waves.

Remarks—Ship was secured by stern and it held steady.

Ship was secured in this manner for all subsequent surveys.

Last drydocking—April 7-9 (1200 hr.), 1946.

FIG. 6. Results of first survey on April 26, 1946.

Weather—Light to heavy rain. Temp. 36° to 52° F. Strong wind.

Sea — $\frac{1}{2}$ to 1 ft. waves.

Remarks—This survey was taken just prior to the passage of depolarizing current. (see Fig. 7)

Last drydocking—April 7-9, 1946.

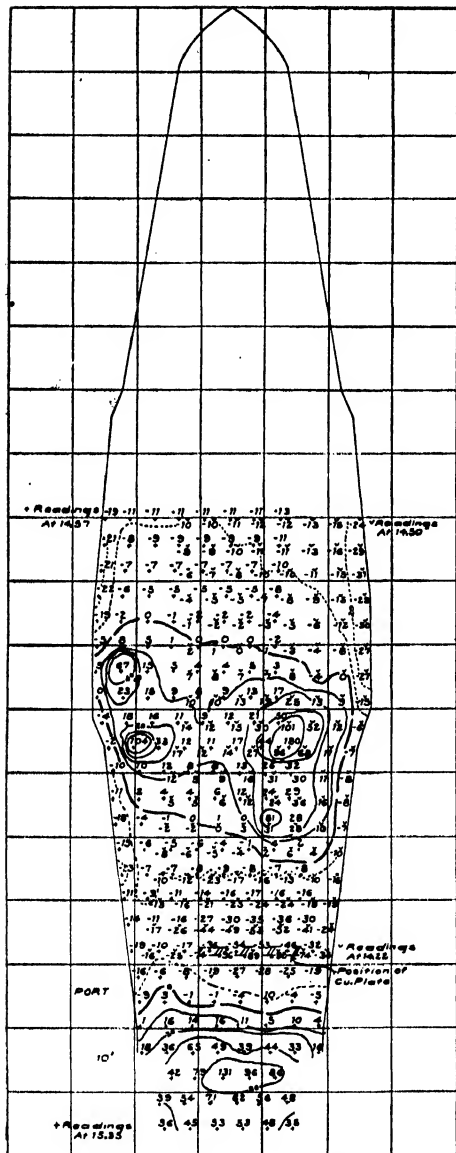


FIG. 7.

FIG. 7. Results of second survey on April 26, 1946.

Weather—Heavy rain. Temp. 36° to 52° F. Strong wind.

Sea — $\frac{1}{2}$ to 1 ft. waves.

Remarks—This survey was taken just after a depolarizing charge of approximately 45 amp-hours had flowed from the hull to a copper plate placed about 32 ft. from the stern.

Last drydocking—April 7-9, 1946.

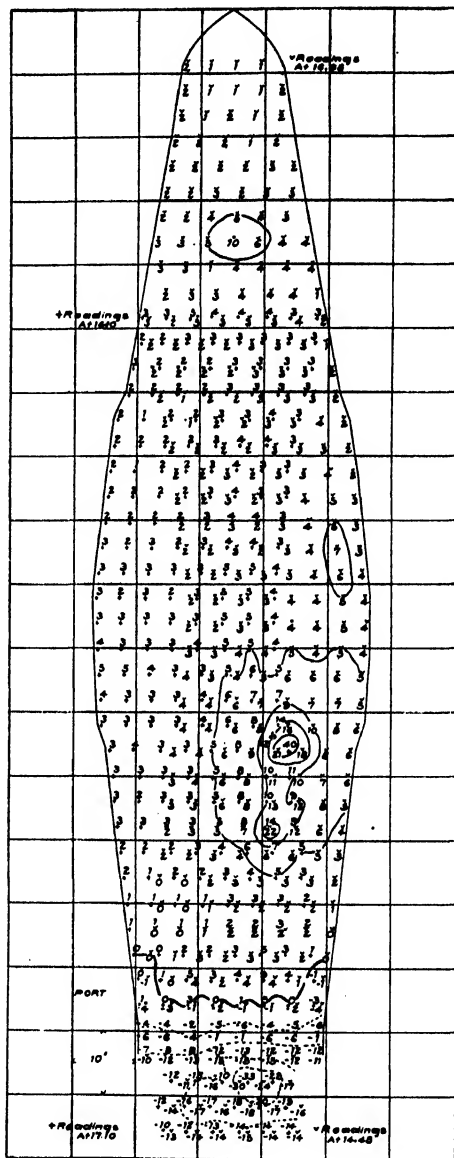


FIG. 8.

FIG. 8. Results of survey on May 18, 1946.

Weather—Light rain. Temp. 40° to 46° F. Strong wind.

Sea — $\frac{1}{2}$ to 1 ft. waves.

Last drydocking—April 30-May 18 (1135 hr.), 1946.

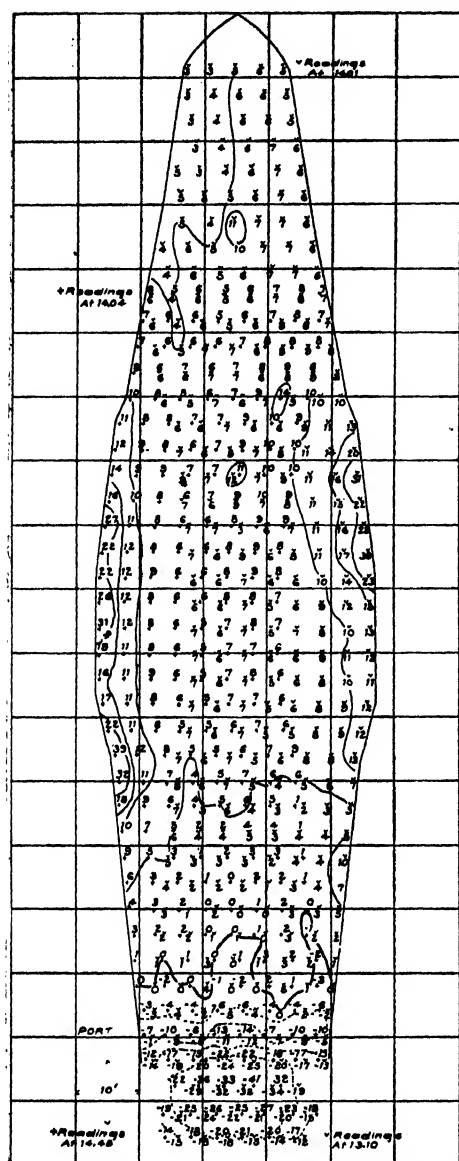


FIG. 9.

FIG. 9. Results of initial survey on May 27, 1946.
 Weather—Overcast with intermittent rain. Temp. 50° to 60° F. Slight breeze.
 Sea—Calm.
 Remarks—Survey made prior to passing of current.
 Last drydocking—April 30-May 18, 1946.

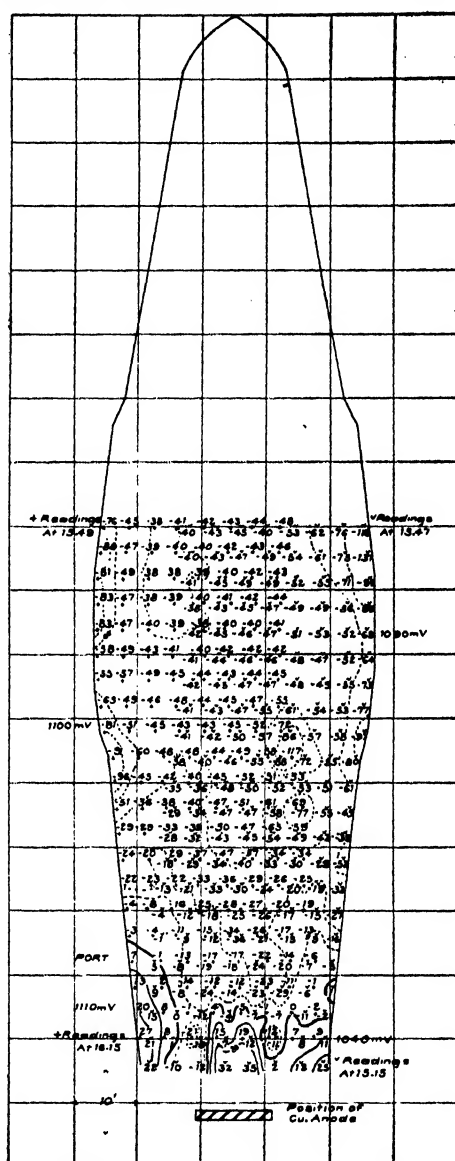


FIG. 10.

FIG. 10. Results of second survey on May 27, 1946.
 Remarks—Survey was carried out while an applied current of about 30 amp. was being passed to the hull from an external anode (copper plate). Also shown is the increase in value of the e.m.f. of the hull with respect to a silver-silver chloride electrode, with time, i.e., passage of current. (The readings were taken using an Avo-Meter 12 v. scale, the hull being connected to the negative terminal of the meter).

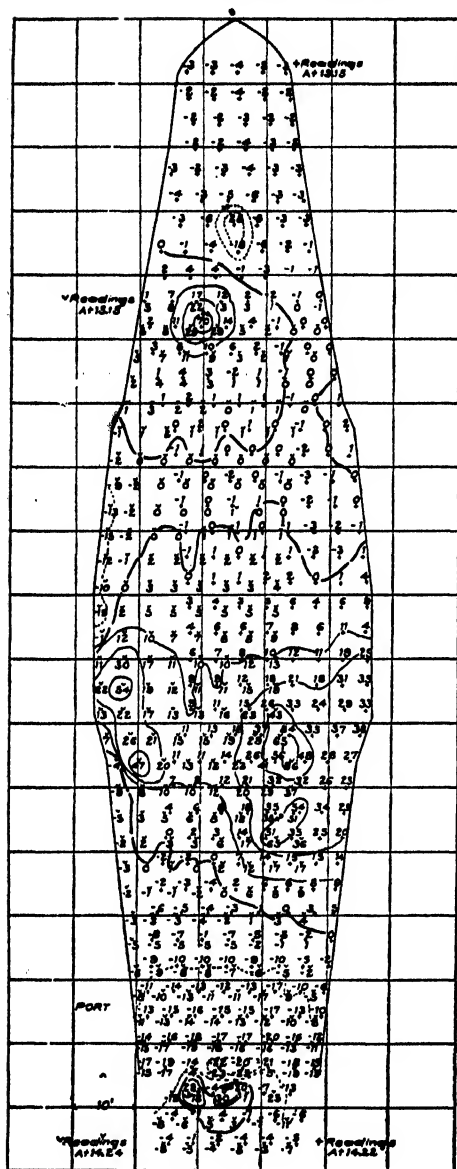


FIG. 11.

FIG. 11. Results of survey on May 30, 1946.
 Weather—Clear. Temp. 45° to 55° F. Light wind.
 Sea—Calm in a.m. $\frac{1}{2}$ ft. waves in p.m.
 Last drydocking—May 29, 1946.

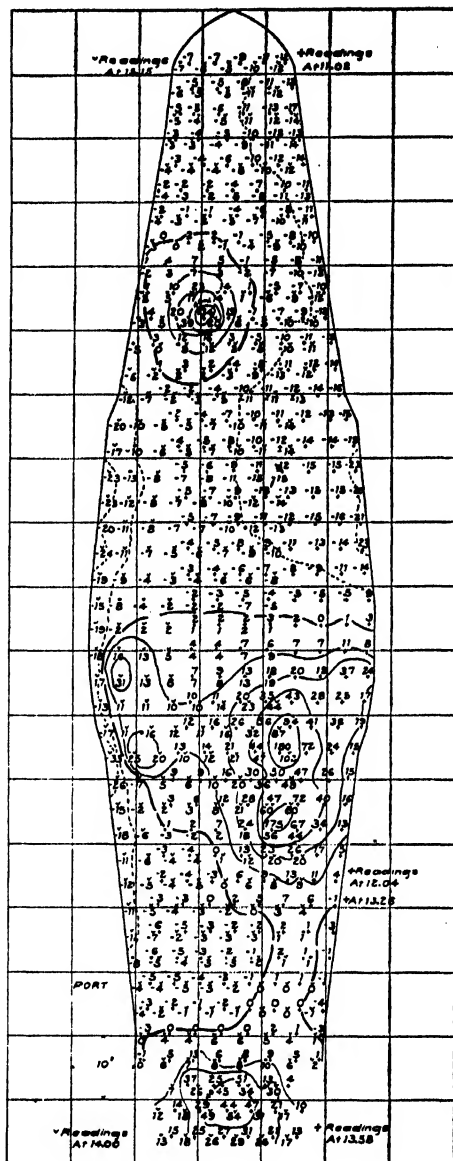


FIG. 12.

FIG. 12. Results of survey on July 2, 1946.
 Weather—Foggy in a.m. Drizzle in p.m.
 Temp. 60° to 70° F. Strong wind in p.m.
 Sea—1 to 2 ft. waves.
 Remarks—Ship had been berthed starboard side next the jetty for a few days since last survey.
 Last drydocking—May 29, 1946.

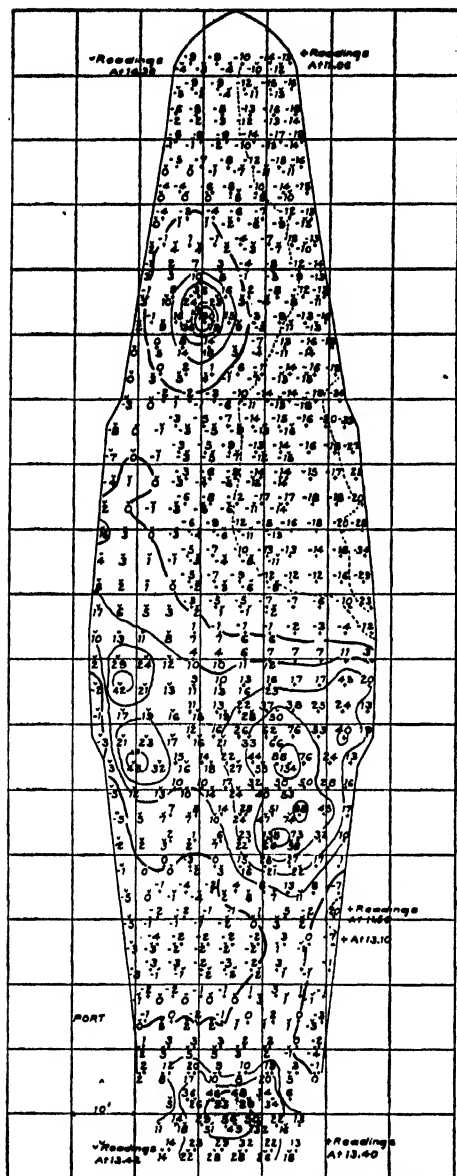


FIG. 13.

FIG. 13. Results of survey on July 4, 1946.
 Weather—Fine. Temp. 60° to 80° F. Slight breeze.
 Sea—Rippled.
 Remarks—The propellers were cleaned by divers on July 3, 1946.
 Last drydocking—May 29, 1946.

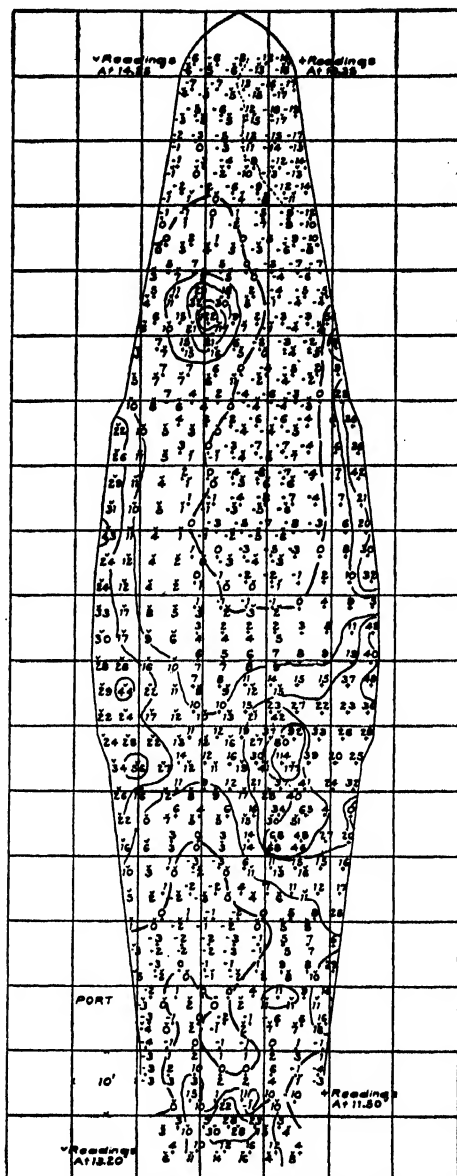


FIG. 14.

FIG. 14. Results of survey on August 2, 1946.
 Weather—Overcast. Temp. 55° to 65° F. Moderate wind.
 Sea—1 ft. waves.
 Last drydocking—May 29, 1946.

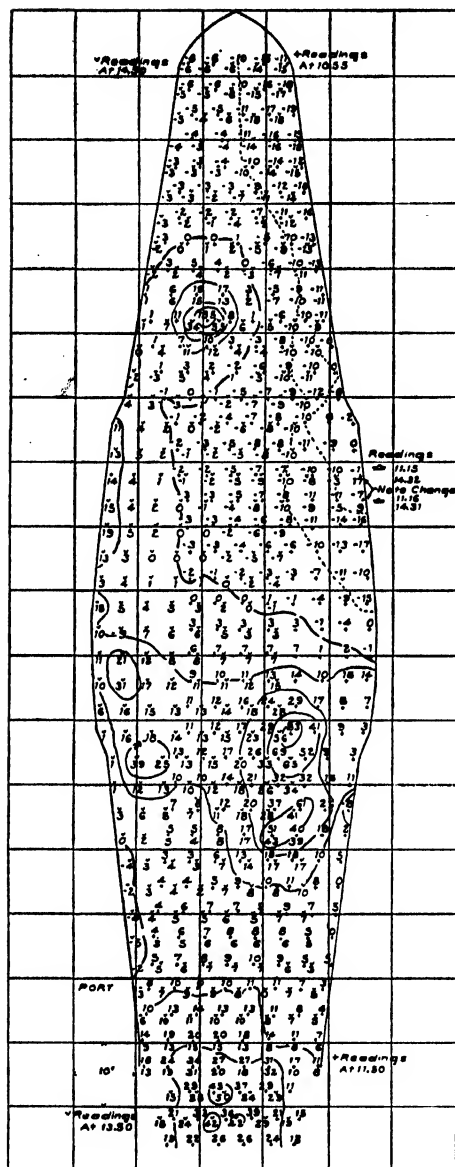


FIG. 15.

FIG. 15. Results of survey on August 5, 1946.
 Weather—Foggy in a.m. Fine in p.m. Temp. 60° to 70° F. Light wind.
 Sea—Calm.
 Remarks—Current of 30 amp. passed for 50 hr. from a copper electrode to hull,
 prior to this survey.
 Last drydocking—May 29, 1946.

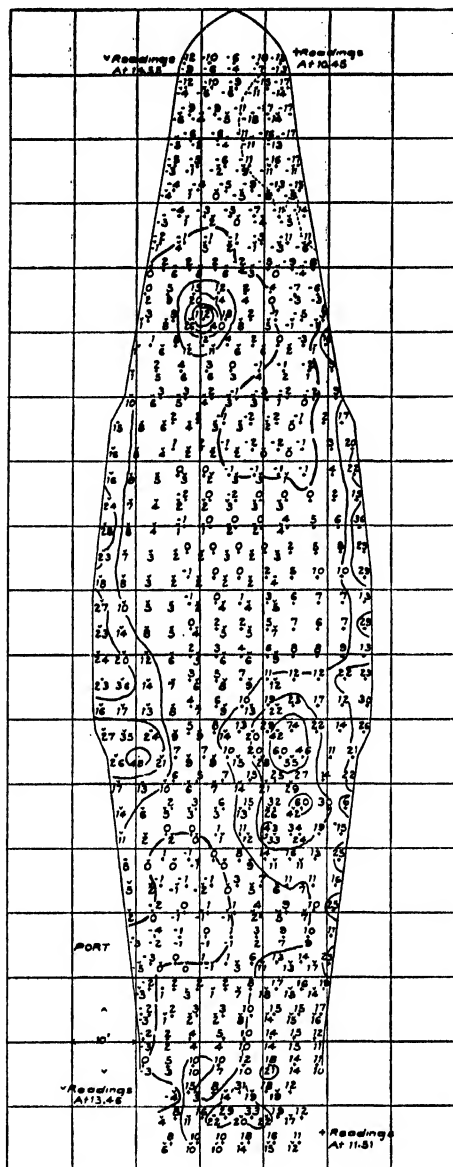


FIG. 16.

FIG. 16. Results of survey on August 12, 1946.
 Weather—Foggy in a.m. Fine in p.m. Temp. 65° to 80° F. Light breeze.
 Sea— $\frac{1}{4}$ ft. waves.
 Last drydocking—May 29, 1946.

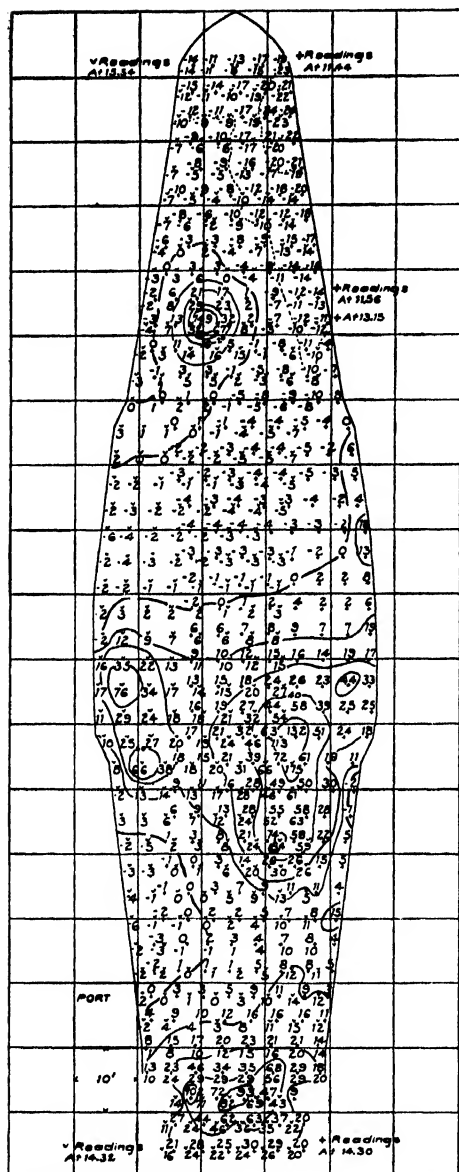


FIG. 17.

FIG. 17. Results of survey on August 14, 1946.
 Weather—Rain. Temp. 55° to 65° F. Light wind.
 Sea—Calm.
 Remarks—The zincs had been cleaned by diver prior to survey.
 Last drydocking—May 29, 1946.

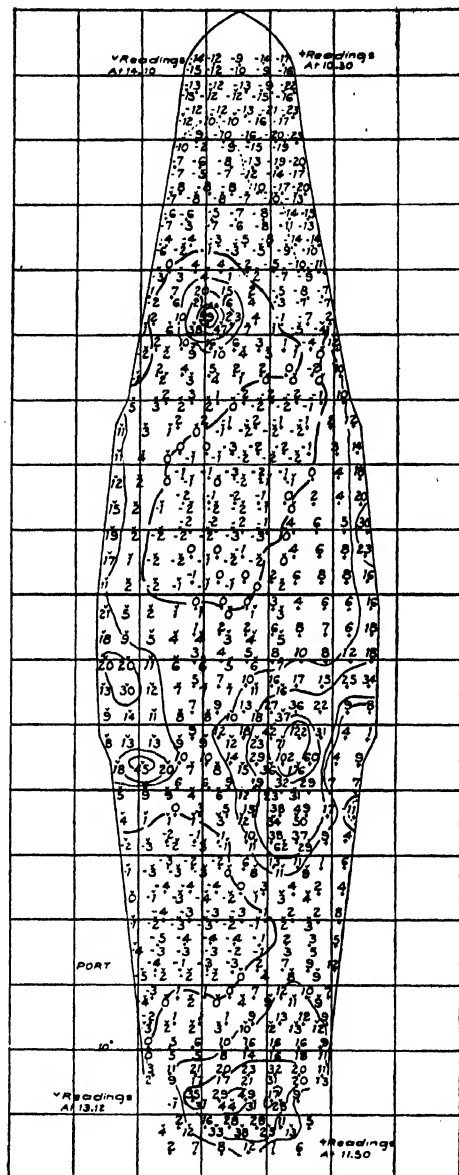


FIG. 18.

FIG. 18. Results of survey on August 21, 1946.
 Weather—Heavily overcast. Temp. 55° to 70° F. Light wind.
 Sea—Calm.
 Last drydocking—May 29, 1946.

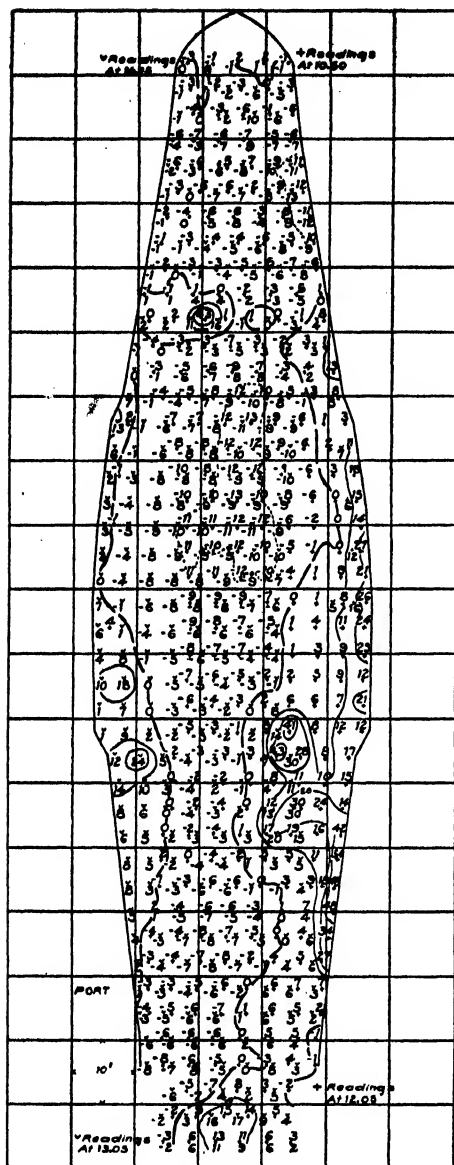


FIG. 19.

FIG. 19. Results of survey on October 28, 1946.
 Weather—Fine. Temp. 45° to 60° F. Moderate wind.
 Sea —1 ft. waves in a.m. $\frac{1}{2}$ ft. waves in p.m.
 Remarks—A dead ship. Decommissioned Oct. 25, 1946.
 Last drydocking—May 29, 1946.

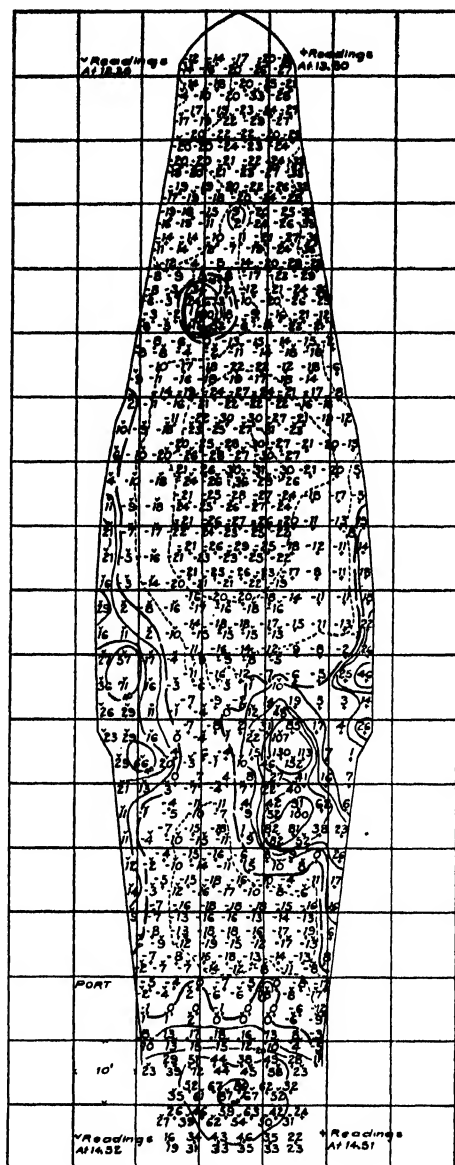


FIG. 20.

FIG. 20. Results of survey on October 30, 1946.
 Weather—Overcast. Temp. 45° to 60° F. Moderate wind, decreasing in p.m.
 Sea —2 ft. waves in a.m. 1 ft. waves in p.m.
 Remarks—A dead ship.
 Last drydocking—October 29-30 (1130 hr.), 1946.

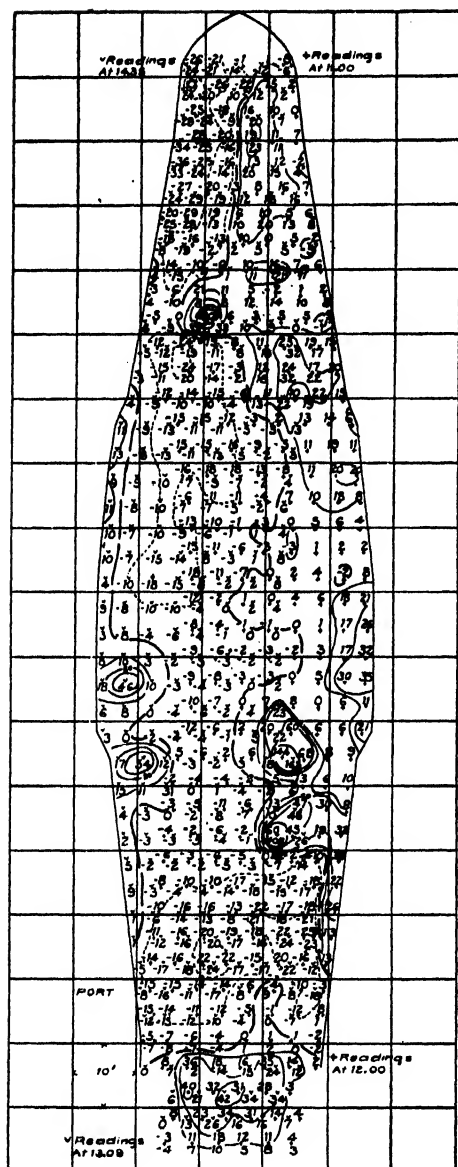


FIG. 21.

FIG. 21. Results of survey on November 1, 1946.
 Weather—Scattered showers. Temp. 40° to 55° F. Strong wind.
 Sea—2 to 3 ft. waves.
 Remarks—A dead ship.
 Last drydocking—October 29-30, 1946.

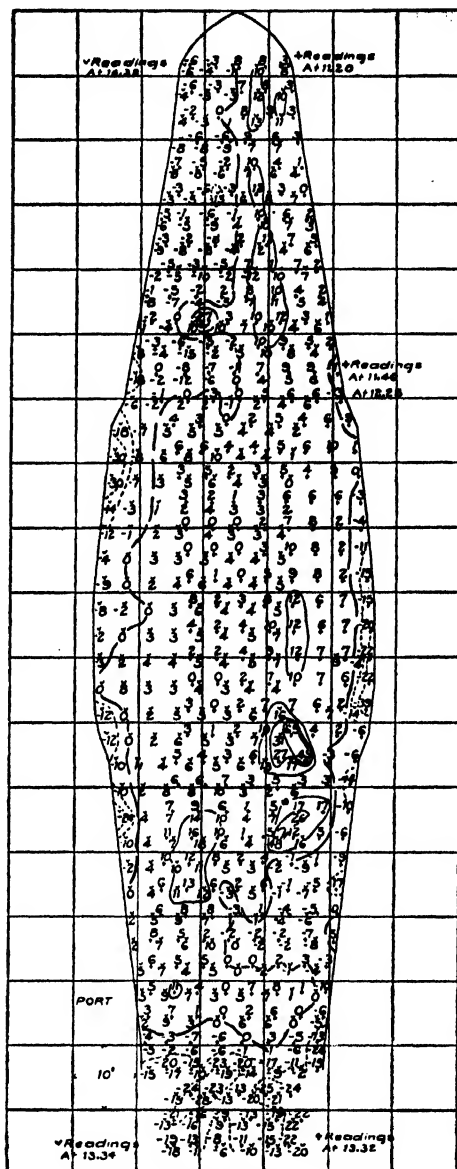


FIG. 22.

FIG. 22. Results of survey on December 11, 1946.
 Weather—Clear. Temp. 35° to 45° F. Strong wind.
 Sea—3 ft. waves.
 Remarks—A dead ship. Had just completed winterization prior to this survey.
 Last drydocking—October 29-30, 1946.

For Figs. 23 to 27 (PLATES I to V) see the following inserts.

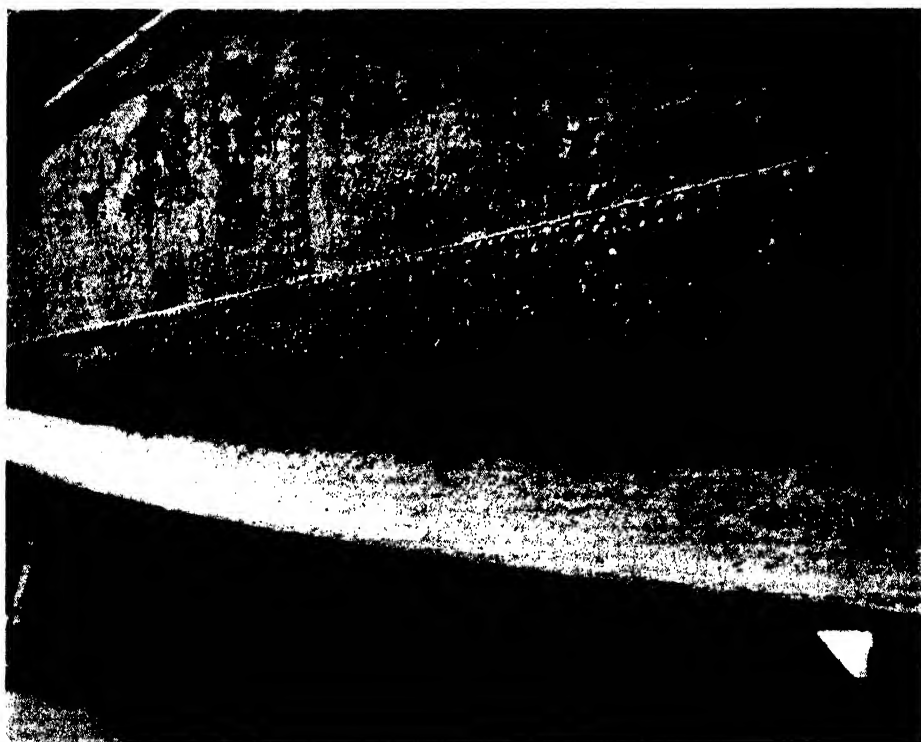


FIG. 23. Showing the general appearance of rusting near water line due to removal of the paint film by abrasion at jetties. Photograph was taken April 7, 1946.

PLATE II

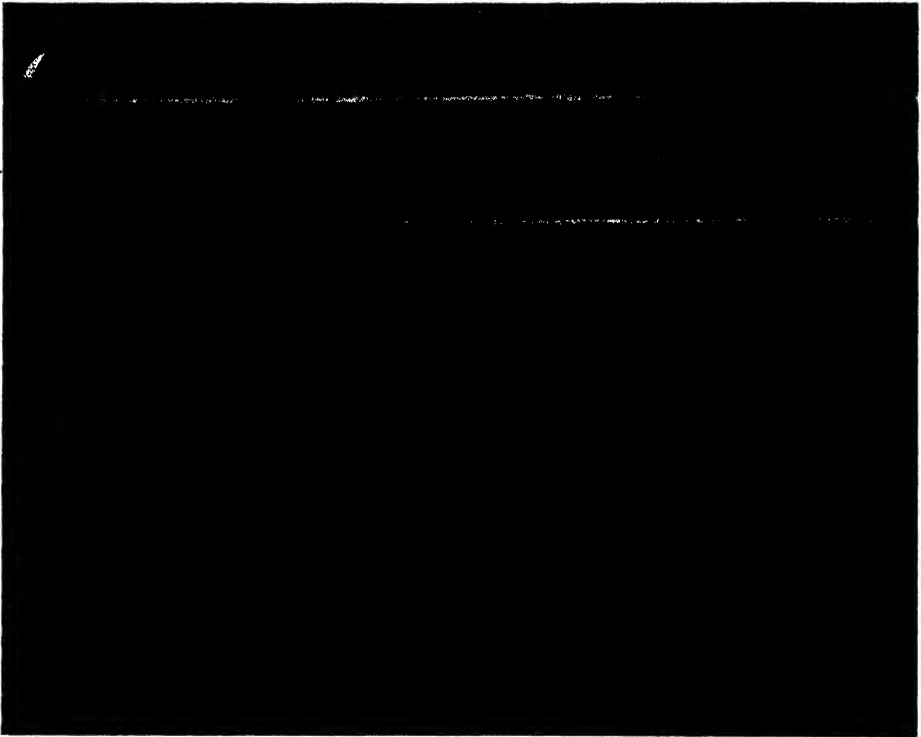


FIG. 24. Showing the general appearance of pitting due to removal of the paint film near the water line by abrasion. Photograph was taken after the hull had been sandblasted and painted with anticorrosive paints.

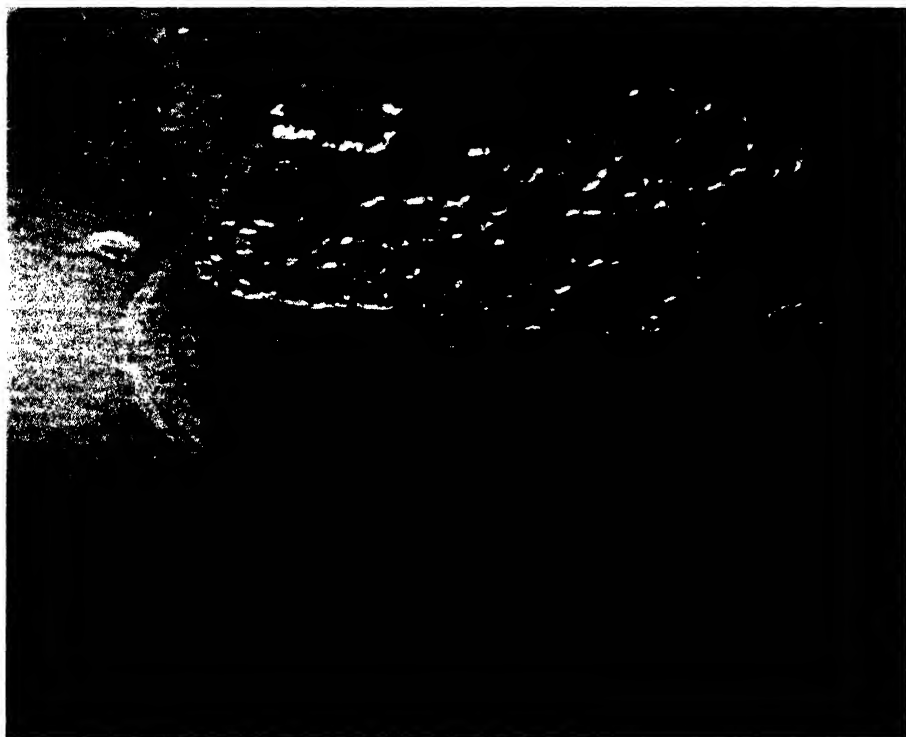


FIG. 25. Showing the general appearance of the severe pitting present at the unpainted bilge block positions prior to May 1946. The photograph was taken after the hull had been sandblasted and painted with anticorrosive paints.

PLATE IV



FIG. 26. Showing the general appearance of rusting at the bow at regions where the paint film had flaked off the hull. This flaking was primarily due to the extreme brittleness of the bituminous paint. Photograph was taken soon after the ship was drydocked on October 29, 1946.

PLATE V

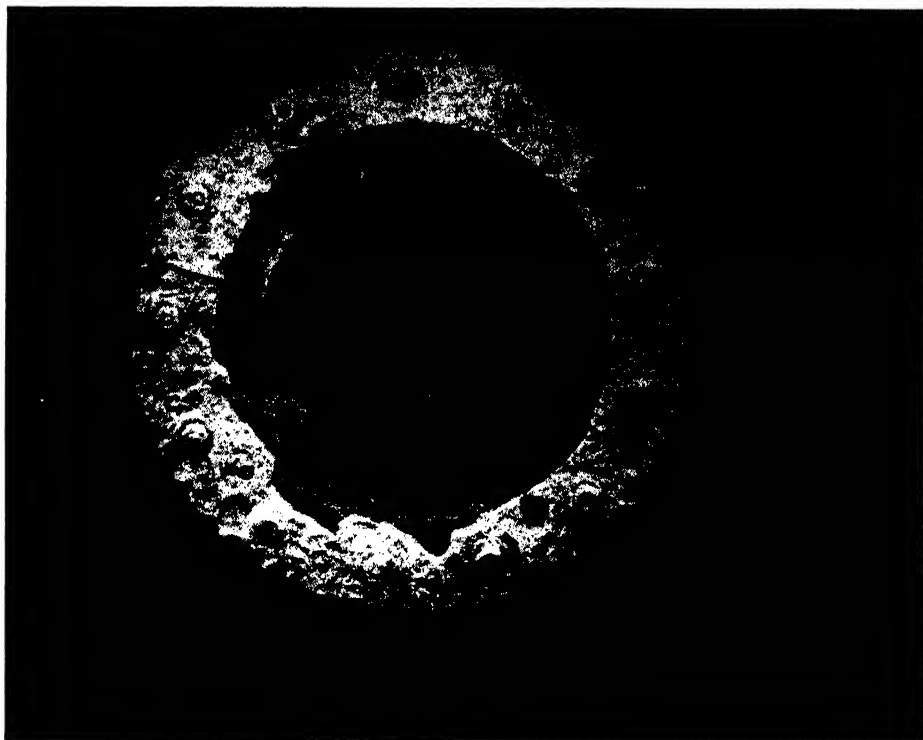


FIG. 27. Showing the general appearance of the zinc anodes at the after magazine flooding valve. Photograph was taken just after the zincs had been cleaned with a small wire hand-brush on October 29, 1946. (+, Studs that had been coated with ozite).

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A 600 KV. ION ACCELERATOR¹

By J. V. JELLEY² AND E. B. PAUL³

Abstract

The 600 kv. ion acceleration equipment that has been developed at the Ottawa Laboratory of the National Research Council is described. Details of ion source, power column, and control gear are given. Using hydrogen a total ion beam of 250 to 300 μ a. was obtained, of which about 80% was atomic ions.

Introduction

In 1944 it was decided to modify the 600 kv. X-ray set in the Ottawa Laboratory of the National Research Council so that it could be used to accelerate positive ions. The equipment was originally built by Dr. G. C. Laurence in 1937 as a source of 600 kv. X-rays for radiographic and therapeutic dosage standardization, and consisted of a voltage-doubling circuit supplying a negative potential of 600 kv. to an accelerating tube, which contained the electron gun and the X-ray target.

High Tension Generator

The voltage doubler is a three-stage circuit of the Cockcroft-Walton type, generating a d-c. voltage approximately six times the peak voltage supplied by the transformer and supplying a maximum current of 5 ma. Six General Electric type KR-5 Kenotrons rated at 200 kv. inverse peak are used, and the filaments are heated by a series of insulating transformers in cascade, the primary of each being fed from the secondary of the previous one. The main 100 kv. transformer is supplied with 0 to 220 v. at 480 c.p.s. from a motor-generator set, the primary voltage being controlled by varying the field current of the alternator with rheostats. The capacities are built up of 0.02 μ f. sections. The total capacity across the output is 0.005 μ f. The voltage ripple therefore was about 3 kv. per ma. The rectifiers were reversed to change from negative to positive potential.

Accelerating Tube

The three-stage accelerating tube is built up of glass cylinders, 28 in. long, 14 in. in diameter, and $\frac{1}{4}$ in. thick, separated by steel disks that support the

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electrodes. The whole is mounted vertically on a steel pumping manifold supported in a steel framework. The joints between the glass cylinders and the steel disks are sealed with Apiezon Q compound. The steel disks are cut away to increase the pumping speed in the upper parts of the tube, and the edges are shielded by corona rings both inside and outside the glass. The coaxial accelerating electrodes and the ion source are connected to the 200, 400, and 600 kv. points on the H.T. set by 500,000 ohm resistors. The brass electrodes are 4 in. in diameter and are chromium plated to reduce sputtering on the glass walls.

The tube was initially evacuated by two Metrovac oil diffusion pumps, types 04B and 02 in series, backed by two Hypervac-20 mechanical pumps in parallel, which gave a pumping speed of approximately 150 liters per sec. of air at 10^{-5} mm. of mercury. Later, in order to be able to enlarge the pumping canal in the ion source, a DPMC-500 oil-diffusion pump was substituted for the 04B pump, and this arrangement increased the pumping speed to approximately 500 liters per sec. A liquid-air trap is built into the pumping manifold near the mouth of the main diffusion pump in order to exclude oil vapor from the main accelerating tube.

The pressure in the main tube is measured continuously in the range 10^{-4} to 10^{-5} mm. of mercury by a gauge of the Philips type (6), and the fore-vacuum pressure between the 02 diffusion pump and the backing pumps is read by a thermocouple gauge. The pressure at the latter point is about 5μ , and the thermocouple gauge has sufficient sensitivity in this range.

The target tube is attached underneath the steel manifold supporting the accelerating tube. The target chamber may be isolated from the main vacuum system by a bronze vacuum-tap consisting of a large tapered straight-through stopcock with a $1\frac{1}{2}$ in. hole through which the ion beam can pass. The small end of the rotating cone of the stopcock is surrounded by a chamber connected to the main vacuum system so that the two parts of the stopcock are pressed tightly together by air pressure in either the open or closed position.

Power Column and Ion Source

Electrical power for the ion source is required at the high potential end of the tube. This is supplied by an alternator driven by an insulating belt from a motor at ground potential. The general layout of the power column is shown in Figs. 1 and 2. The stack consists of a Dilecto cylinder, $7\frac{1}{2}$ ft. long, 3 ft. in diameter, and $\frac{1}{4}$ in. thick, mounted on a steel framework and supporting a plywood electrode, approximately 5 ft. in diameter and $\frac{1}{8}$ in. thick. This electrode was fabricated* in one piece by building up the plywood on a wooden form and then baking the glue in a large oven. The electrical components are mounted on a steel framework which rested on a floor within the electrode. The electrode is painted with a "Dag" preparation consisting of colloidal graphite suspended in an organic solvent.

* This construction was carried out in the Structures Laboratory of the National Research Council.

Mounted inside the electrode are a 2 kva. alternator driven by a rubber V-belt from a 5 h.p. motor at floor level, a 30 kv. full wave rectifying set with four 0.01 μ f. condensers in parallel, which supplies 30 ma. d.c. for the discharge tube, the control gear for the set, and for the heater of the palladium

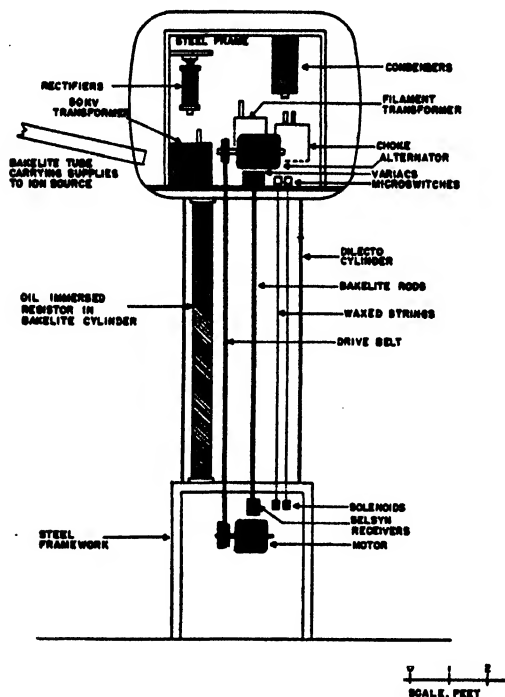


FIG. 1. Sketch of the power column.

tube that admits hydrogen or deuterium to the discharge tube. This leak was mounted directly on the ion source inside an aluminum spinning at the top of the accelerating tube and is of all-metal construction. The leak (designed by Dr. H. M. Cave) consisted of two palladium thimbles hard-soldered inside a steel envelope. The hydrogen line to this leak from the hydrogen supply at the base of the power stack, as well as the electrical supplies from the power stack, are taken from the power column electrode to the ion source through a bakelite tube.

A sketch of the ion source as finally used is shown in Fig. 3. The operation of this type of source has been described by Oliphant and Rutherford (5) and others (2, 3). The ring of metal inside the porcelain insulator keeps the minimum distance between the electrodes less than the mean free path of the electrons in the gas at the working pressure of the discharge tube. This precaution reduces the possibility of breakdown at this point. It also shields the porcelain surface, since a breakdown across this surface generally produces a semiconducting path along which breakdowns would occur more and more

frequently. The centering of the inner electrode is very critical and has to be correct to about 0.001 in.

The final design of the cathode block of the ion source was adopted after trials of other designs. The first model ended in a toroidal steel block with

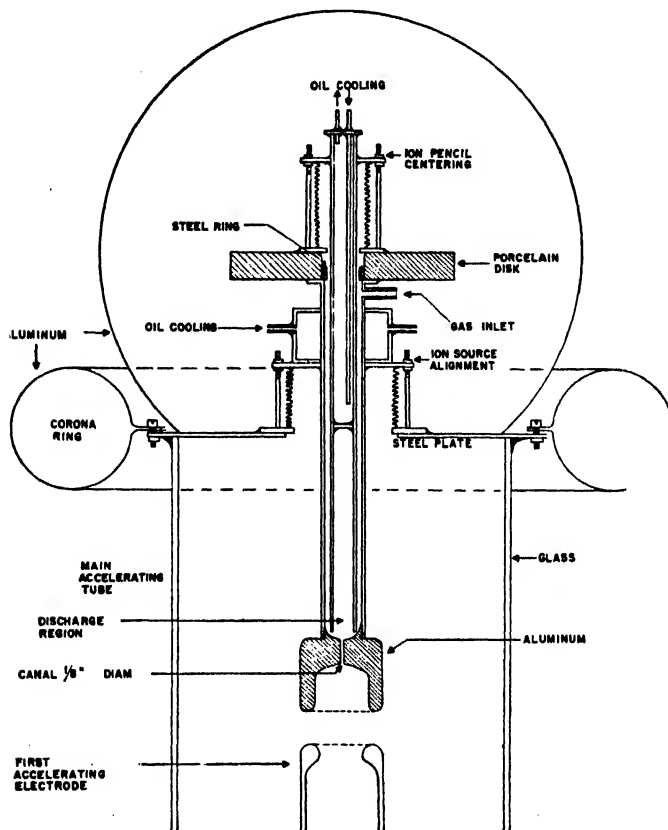


FIG. 3. Sketch of the ion source.

the lower end of the canal less than $\frac{1}{2}$ in. from the surface of the "lens." The toroid was about 1 in. smaller diameter than the electrode that it faced. With this arrangement a considerable part of the ions emerging from the canal were lost after undergoing the first acceleration. The later model (designed by Dr. H. M. Cave) was intended to allow the ions to emerge first into a relatively field-free region and then to be focused by a symmetrical "lens." This served to focus a larger part of the output of the ion source and resulted in a narrower beam and a higher beam current at the target. The diameter of the beam at the target was approximately 0.5 cm. Aluminum is used for the end surface of the ion source to reduce the X-rays produced at this point by secondary electrons accelerated up the tube. The pumping canal shown is that used with the 500 liters per sec. pumping system; with the lower pumping speed a canal half the diameter was used. The ion source is

PLATE 1

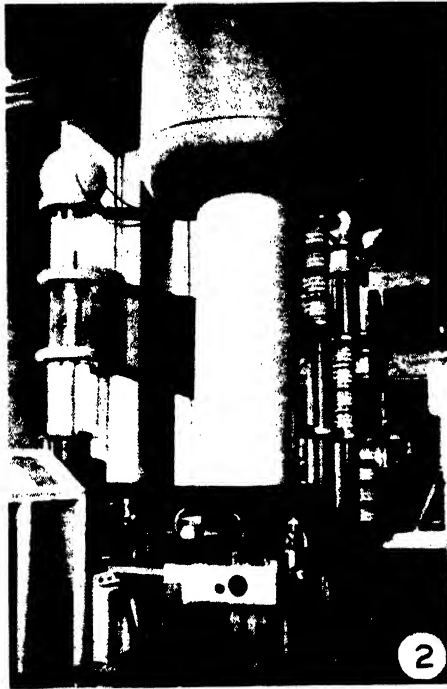


FIG. 2. *Photograph of the ion accelerator, with the power column in the foreground.*



FIG. 4. *Photograph of the control desk of the ion accelerator.*



FIG. 5. *Photograph of the neutron monitor.*

cooled by transformer oil continuously circulated from the ground level through bakelite and neoprene tubes; the oil itself was cooled at ground level in a tank by a copper spiral through which water circulated.

The main accelerating potential is measured by a 7 ft. resistor mounted inside the power column stack. It was constructed of about 500 two-megohm standard ceramic sealed 1 w. carbon resistors arranged in a helix around a bakelite cylinder of diameter 2 in. This was mounted inside a 4 in. Dilecto cylinder filled with transformer oil. This oil was at first circulated. However this was found to be unnecessary as a coolant and the simpler arrangement of static oil as an insulator was adopted. The voltage across 1/3000 of the main resistor is measured by a bridge method in which this small fraction of the total voltage is balanced against a similar voltage from a power supply. The method has the advantage that an accurate robust meter can be used. The voltage-measuring equipment was calibrated by means of the γ -ray resonances from protons on lithium and fluorine.

Controls

Whenever the accelerated beam of ions strikes part of the accelerating tube, secondary electrons are liberated and accelerated up the tube. These give rise to X-rays on striking the ion source and other metal parts within the tube. The dosage received around the base of the tube and power stack was found to be several hundred times the tolerance dose per day. This made it necessary to place all controls behind a 13 in. cement wall about 50 ft. from the accelerating tube.

All controls are mounted on a desk-shaped panel, which is shown in Fig. 4. The controls on the 30 kv. set and the palladium tube leak heater in the power-stack electrode are turned directly through 8 ft. bakelite shafts by Selsyn motors (General Electric Type 2JD5H1) driven from corresponding motors mounted behind the control desk.

If the current through the Philips gauge exceeds a certain value (i.e., the pressure exceeds a certain value) it lowers the bias on a valve that actuates a relay that turns off the high voltage.

Monitoring Equipment

One purpose of the equipment was to provide strong sources of neutrons from the (d, n) type of reaction. A monitoring system was therefore desired that would give a continuous reading of the fast neutron flux during an experiment. For this facility a long, thin-walled copper counter filled with boron trifluoride gas was employed and was operated in the proportional region so that it was insensitive to relatively high γ -ray backgrounds that might be present. This type of neutron monitor has been described by Hanson and McKibben (4), who have found the sensitivity of their instrument to be reasonably constant for neutrons of energy between 10 kev. and 5 Mev. They quote a result by R. F. Taschek that indicates a falling-off in sensitivity

by 60% at 16 Mev. The counter that we used was of length 24 in. and diameter 0.5 in. and was mounted along the axis of a paraffin-wax cylinder of diameter 6 in. and length 24 in., the whole being sheathed in a cadmium skin to exclude slow neutrons scattered from nearby objects. The monitor was mounted on an adjustable holder attached to a table (see Fig. 5) and could be "aimed" at the target. The table also carried the electrical equipment which consisted of stabilized power supplies, filter unit, amplifier and a circuit for integrating the pulse rate. This provided a d-c. output proportional to the neutron flux, which was displayed on a meter on the control desk so that relative values of the flux level could be recorded during experiments. The pulse-rate integrating circuit is shown in Fig. 6.

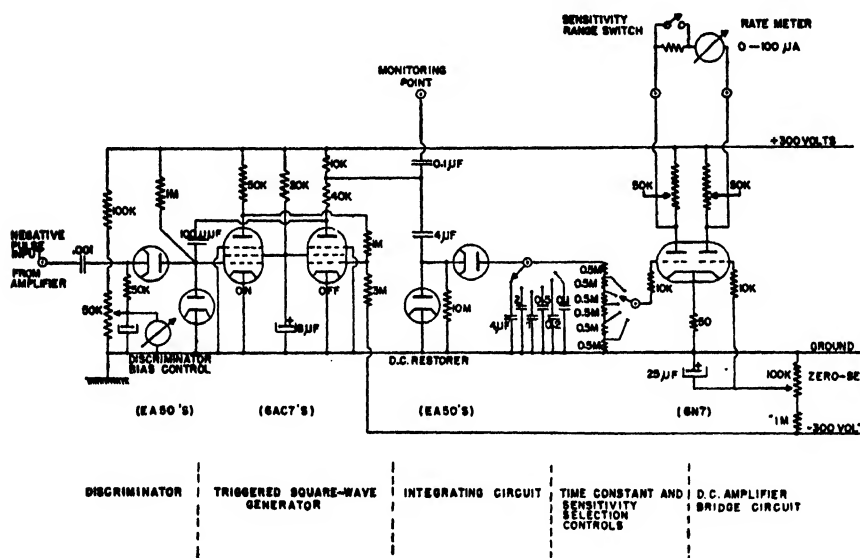


FIG. 6. Circuit diagram of the pulse-rate integrating meter.

The equipment can also provide a strong source of γ -rays from (p, γ) reactions; these were monitored by a suitable Geiger-Müller counter, the output pulses being supplied to the rate-meter circuit as for the neutrons. The counter, placed close to the target, was heavily shielded by lead to reduce to a minimum the background counts produced by X-rays from the set.

Owing to the unsafe X-ray intensities present in the main room, all recording apparatus such as scaling units and oscilloscopes had to be in the control room. The effective cable-lengths between the detecting devices (ion chambers, counters, etc.) at the target and the control room being 50 ft., it was necessary to supply electrical units for satisfactory distortion-free transmission of pulses from the apparatus near the target to the recording equipment. Each unit, one situated near the target and one at the control desk, is provided with five channels for carrying five independent connections if necessary. Each

channel of the "transmitter" unit contains a phase inverter and a cathode-follower so that pulses of either sign can be introduced and transmitted at low level down the respective cable. Each channel of the "receiver" unit contains one tube operated as a phase-splitter so that pulses of either sign can be made available to the recording gear.

Performance

With the small pumping canal in the ion source running on hydrogen the total current on the target was from 80 to 100 μ a. A rough magnetic analysis at the target showed that about 80% of the ion beam was atomic, in agreement with the early observations on this type of source (5). When the canal was enlarged to $\frac{1}{8}$ in. diameter the total current was increased to 250 to 300 μ a. Voltage stability was around 1%. However, the inhomogeneity of ion energy was much greater since an ion source of this type produces ions with a total spread of about 25 kv. The neutron intensities produced by bombarding various targets with 600 kv. deuterons and comparing the count in the neutron monitor with that produced by a Ra-Be source are as follows:

D ₂ O + P ₂ O ₅ target	250 mc. equivalent per μ a.
Be metal target	600 mc. " " "
Li metal target	500 mc. " " "

The yields for beryllium and D₂O + P₂O₅ targets are in agreement with the yields found by Amaldi, Hafstad, and Tuve (1), but our measured yield for lithium is about 40% lower, which difference may be due to the decreased sensitivity of our neutron monitor at high neutron energies.

The γ -ray yield from a lithium metal target bombarded by the unresolved beam of 600 kv. protons was measured by a calibrated "thick-walled" ionization chamber and was found to be of the order of 10^{-2} mc. per μ a.

Acknowledgments

This work was done in the British-Canadian Atomic Energy Project under Dr. J. D. Cockcroft, and was initially under the immediate direction of Dr. W. E. Burcham and, after September 1945, of Dr. H. M. Cave. The valuable help of Mr. J. W. McKay and the excellent technical assistance of Mr. P. S. Lamb are gratefully acknowledged.

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THE OXIDATION, IGNITION, AND DETONATION OF FUEL VAPORS AND GASES

VII. THE OXIDATION OF PENTANE IN VARYING CONCENTRATION IN AIR AT TEMPERATURES RISING TO 700° C. AND THE EFFECT OF IRON CARBONYL ON REACTION VELOCITY¹

BY R. O. KING²

Abstract

Results are given for the oxidation in reaction chamber No. 10 of pentane mixed with air, mixture strength being varied from 25% weak to 100% rich. Oxidations were carried out with and without additions of iron carbonyl to the pentane. The experiments were made mainly to find a rational explanation for the antiknock property of rich fuel-air mixtures. The experimental results for undoped mixtures show that, at temperatures approaching those of the end gas in an engine, reaction velocity increases by 100% on increasing mixture strength over the range mentioned above and by 100% on increasing temperature from 600° to 650° C. Similar increases in reaction velocity with rise of temperature and with increase of mixture strength were obtained for the doped mixtures over the high temperature range but at temperatures 150° C. lower than for undoped mixtures. The characteristics of the experimental results confirm the conclusion reached in earlier Parts, namely, that oxidation of pentane in the conditions of the experiments is a heterogeneous reaction.

Introduction

It has been shown by experiments already described (1, 2, 3) that oxidations of pentane and hexane can be carried out in reaction chamber No. 10, without explosion, at whatever temperature may be required for completion of reaction. The experiments, with one exception, were made when using mixtures of combining proportions with air. Their oxidation characteristics are described in the references quoted and experimental evidence given showing that detonation in an engine is delayed or prevented by dilution of the end gas with oxidation products (3).

The liability of a fuel-air mixture to detonate varies with mixture strength, and the experiments to be described in this Part were made to determine the oxidation characteristics of weak and rich mixtures, in particular to ascertain the fundamental reason for the antiknock property of rich mixtures which is of importance in practice.

Experimental Arrangements

The No. 10 reaction chamber used for the experiments was of Jena Supramax glass and of the dimensions given in Part I (1). Pentane, taken as before, as a representative liquid paraffin hydrocarbon was used to form mixtures with air in varying proportions. The pentane and the methods of measurement were as described in the appendix to Part I.

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Contribution from Defence Research Board, Ottawa, Canada.

² Research Scientist, Naval Division, Defence Research Board, lately Director of Scientific Research and Development, Royal Canadian Navy.

The rate of air supply to the reaction chamber in cubic centimeters per minute was measured at room temperature and the pentane added as liquid in conditions ensuring that vaporization was complete before the mixture entered the chamber.

A pentane-air mixture is defined as being weak or rich according to the percentage by which the pentane constituent is less or greater than that required for combining proportions.

Thus,—

Combining proportions mixture is $C_5H_{12} + 8 O_2 + 30.3 N_2$

100% rich mixture is $2C_5H_{12} + 8 O_2 + 30.3 N_2$

25% weak mixture is $0.75C_5H_{12} + 8 O_2 + 30.3 N_2$

A combining proportions mixture of pentane with air would, according to kinetic theory, contain 2.87% only of pentane vapor. Rates of mixture supply given in the text are to be taken as rates of air supply plus whatever addition of pentane vapor is required for the stated mixture strength.

Rates of oxygen reacted as given by the graphs are for pentane-air mixtures; the proportion of nitrogen is omitted from the stated composition.

Percentage concentrations of iron carbonyl stated in the text are in respect of the pentane constituent of the pentane-air mixture, the carbonyl being added as liquid to the pentane prior to vaporization.

Temperatures of reaction are taken as indicated by the "inside" thermocouple resting on the top of the reaction chamber (1, pp. 333-334).

Experimental Results

Flow configuration is the major factor determining rate of oxidation (2) and in reaction chamber No. 10 may be such that reaction is so rapid at some temperatures that measurement of rate is difficult. The configuration in the chamber is fixed by rate of mixture supply and the diameter of the admission orifice; factors which determine degree of turbulence and the velocity with which the reacting mixture impinges on the active surface. If the rate of mixture supply is too small and the diameter of the orifice too large, the velocity of the jet may not be sufficient to ensure deposition of metal rather than of metallic oxide on the surface of the chamber when the mixture contains a metallic dope such as iron carbonyl.

On the other hand, if the velocity of the jet is increased sufficiently to ensure deposition of metal on the surface of the chamber, flow configuration conditions arise which increase reaction velocities in rich mixtures to such an extent that measurement may be extremely difficult. The difficulty of choosing a suitable flow configuration is illustrated by the series of experiments described in succeeding paragraphs.

Rates of oxidation observed for the flow configuration due to passing a combining proportions pentane-air mixture through the 1.0 mm. orifice at 50 cc. per min. are given by the graphs of Fig. 1. It will be noted that iron

carbonyl in the concentration of 1.0% increases rate of reaction at all temperatures, the aldehyde hump not being eliminated on the addition of the dope, as in earlier experiments. The failure of iron carbonyl to inhibit aldehyde formation was attributed to the jet velocity being insufficient to ensure deposition of metal on the active surface of the reaction chamber, and the velocity

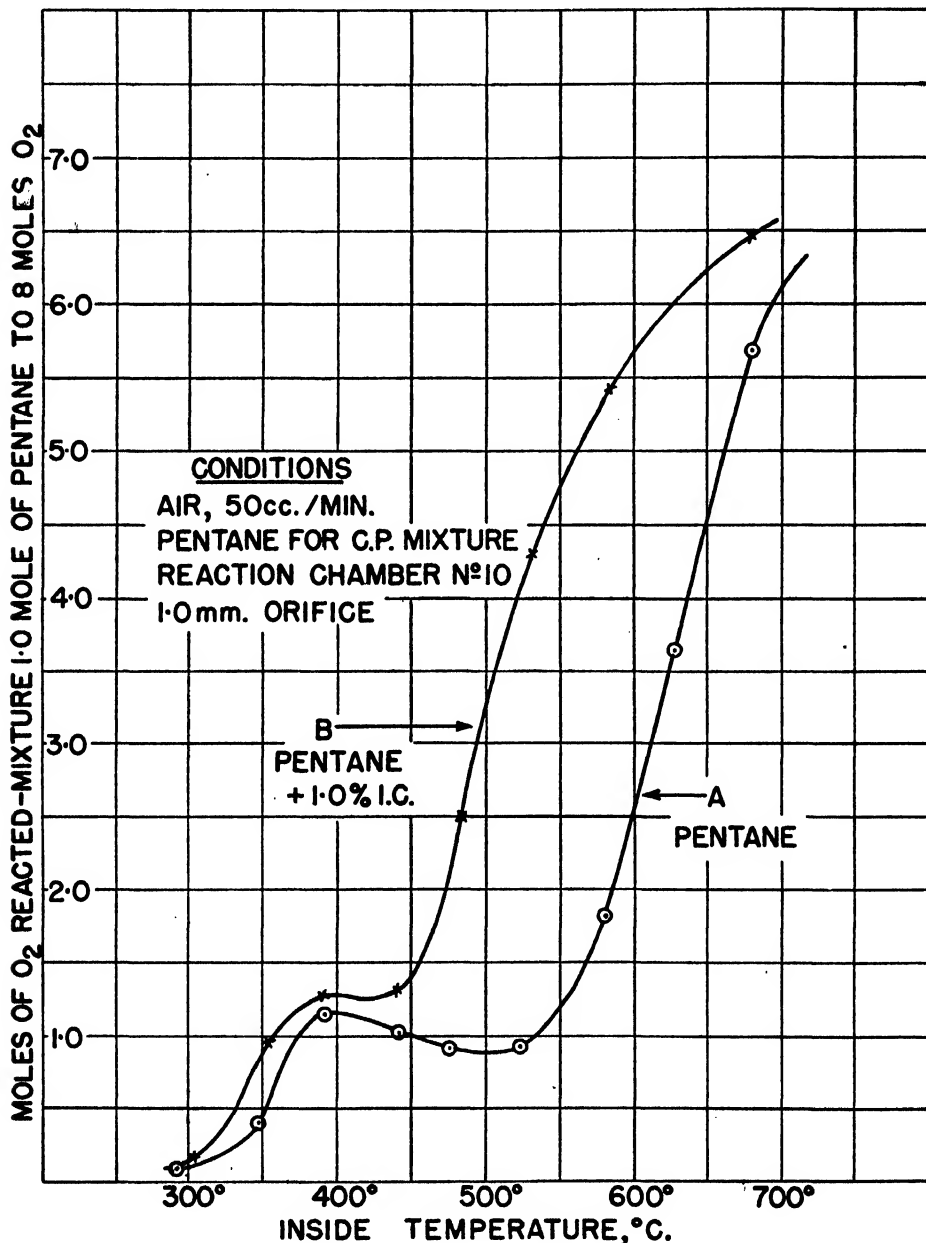


FIG. 1. Rates of oxygen reacted, pentane and pentane plus iron carbonyl for the flow configuration due to supplying a combining proportions mixture with air at 50 cc. per min.

was increased by raising the rate of mixture supply to 75 cc. per min. The experimental results then obtained are given by the graphs of Fig. 2. It will be noted, graph *B* of the figure, that the aldehyde hump has disappeared. Comparing graph *B* with the similar graph of Fig. 1, it will be seen that a

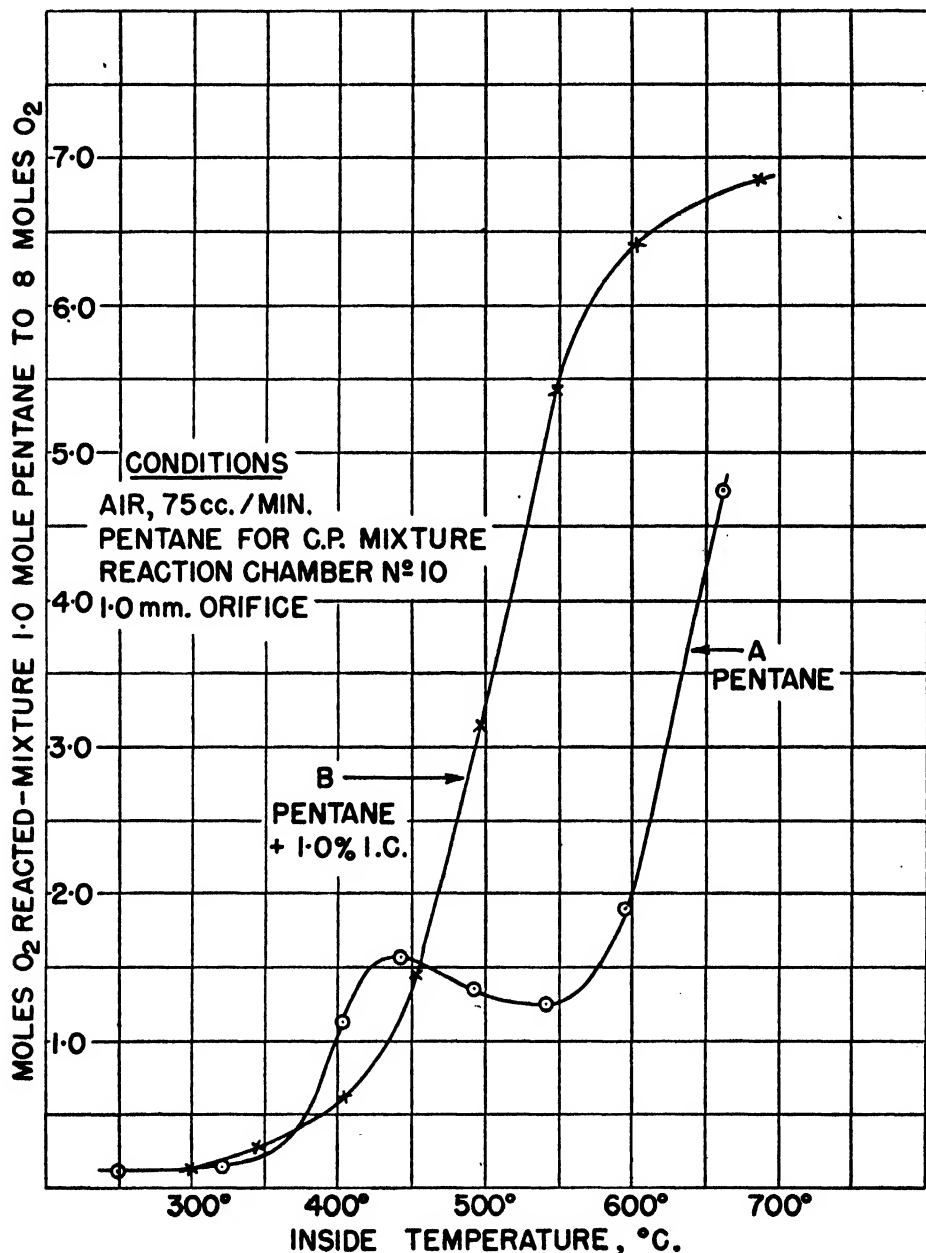


FIG. 2. Rates of oxygen reacted, pentane and pentane plus iron carbonyl for the flow configuration due to supplying a combining proportions mixture with air at 75 cc. per min.

higher rate of oxidation at temperatures above 450°C . is obtained on increasing rate of mixture supply of the *doped mixture* from 50 cc. to 75 cc. per min. On the other hand, a comparison of graphs *A* of Figs. 1 and 2 shows that, for *undoped* pentane, rate of oxidation at high temperatures diminished with increase in rate of mixture supply.

The experiments described above indicated that the flow configuration fixed by a mixture supply of 75 cc. per min. was to be preferred to that given by the lower rate of 50 cc. per min. if the characteristic effect of the dope to inhibit aldehyde formation were to be obtained. It then remained to determine rates of oxidation in the conditions if pentane were mixed with air greatly in excess of the proportion required for a "correct" mixture. The results of an experiment made accordingly are given by the graphs of Fig. 3.

Graph *A* of the figure shows that even for pentane undoped, reaction velocity was so great in a 100% rich mixture, over the temperature range 350° to 390°C . and again over the range 600° to 650°C ., that observations were not obtained. Graph *B* of the figure obtained when the pentane contained iron carbonyl in the concentration of 1.0% shows a similar high reaction velocity over the high temperature range but at temperatures approximately 150°C . lower, reaction of the oxygen being substantially complete at the relatively low temperature of 550°C .

Rates of formation of carbon oxides are of interest. The graphs of Fig. 5 show that for the doped pentane, rate of formation of carbon monoxide was inappreciable, reaction being substantially to carbon dioxide and steam at any temperature. On the other hand, the graphs of Fig. 4 for pentane undoped show a rapid increase in rate of carbon monoxide formation over the temperature range above 600°C . It was demonstrated by the experiments described that reaction occurred at inconveniently high velocity when 100% rich mixtures were used.

The object of the experiments described above was to fix conditions suitable for experiments in which mixture strength would be the sole variable over the widest practicable range. It was concluded that suitable flow configuration would be set by passing the mixture through a 1.0 mm. orifice at 75 cc. per min. and that reaction velocity might not be too great if a maximum mixture strength of 50% rich were used.

Reaction velocities for a combining proportions mixture obtained when the rate of mixture supply was 75 cc. per min. are given by the graphs of Fig. 2, and the experiments were concluded by oxidations of mixtures 25% weak and 50% rich. The doped combining proportions mixture contained iron carbonyl in the concentration of 1.0% in the pentane, and, in order that the substance might be supplied to the reaction chamber at a constant rate irrespective of mixture strength, concentrations of 1.33% and 0.67% respectively in the pentane were used in the weak and rich mixtures. The experimental results are given by the graphs of Figs. 6 to 9, Nos. 7 and 8 giving rates of formation of the carbon oxides for the weak mixture. Similar graphs for the 50% rich mixture are largely duplicates of those of Figs. 4 and 5 for the 100% rich mixture and are not given.

Discussion of Experimental Results

The preliminary experiment, Fig. 1, made to determine a favorable rate of mixture supply for subsequent measurement of the effect of mixture strength on reaction velocity, discloses that conditions can be obtained in which a metallic

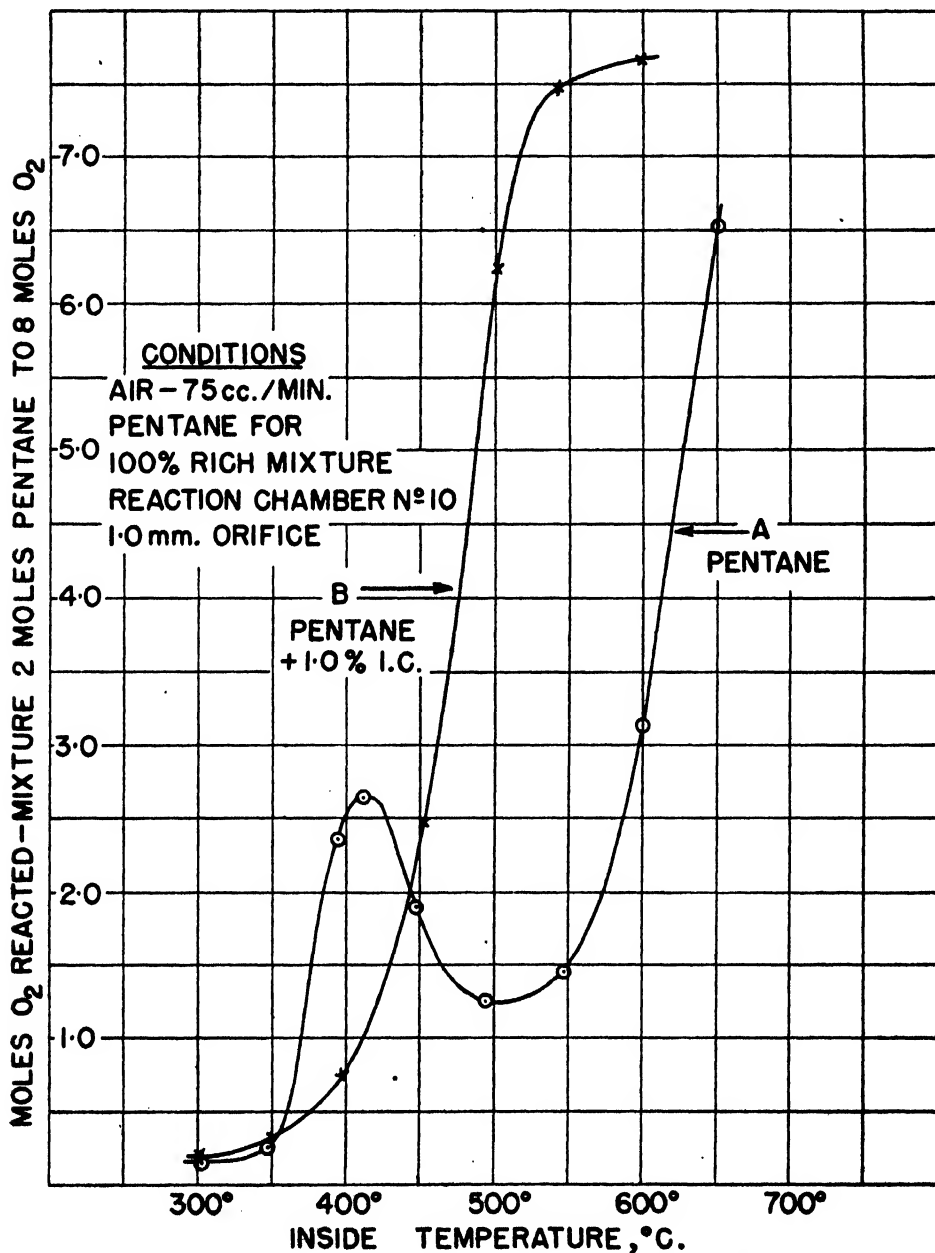


FIG. 3. Rates of oxygen reacted, 100% rich pentane-air mixture, with and without iron carbonyl, for flow configuration fixed by supplying the mixture at 75 cc. per min.

dope such as iron carbonyl promotes oxidation at all temperatures of reaction. The flow configuration consequent on supplying reacting mixture to the reaction chamber at an unusually low rate, through a relatively large orifice, was such that with the doped mixture the active surface was mainly coated with iron oxide instead of with metal as found in earlier experiments when

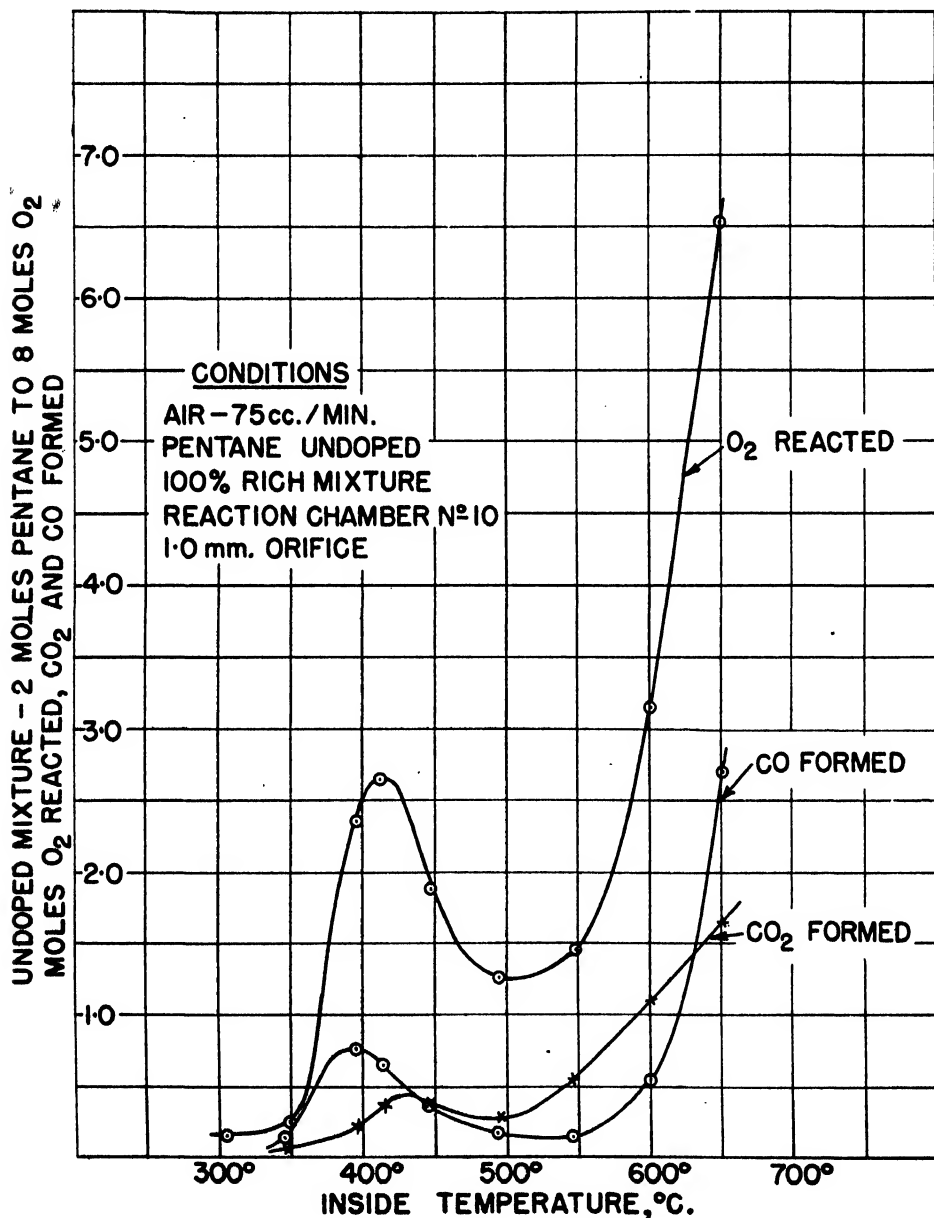


FIG. 4. Rates of formation of carbon oxides, 100% rich undoped pentane-air mixture supplied at 75 cc. per min.

using higher rates of mixture supply. The experimental results show that reaction to aldehyde as indicated by the hump on graph *B*, Fig. 1, proceeds at a higher rate on the oxide coated surface than on the clean glass surface, graph *A*, Fig. 1. The experiments show that iron oxide is most active to promote aldehyde formation when freshly formed. Thus referring to Part III

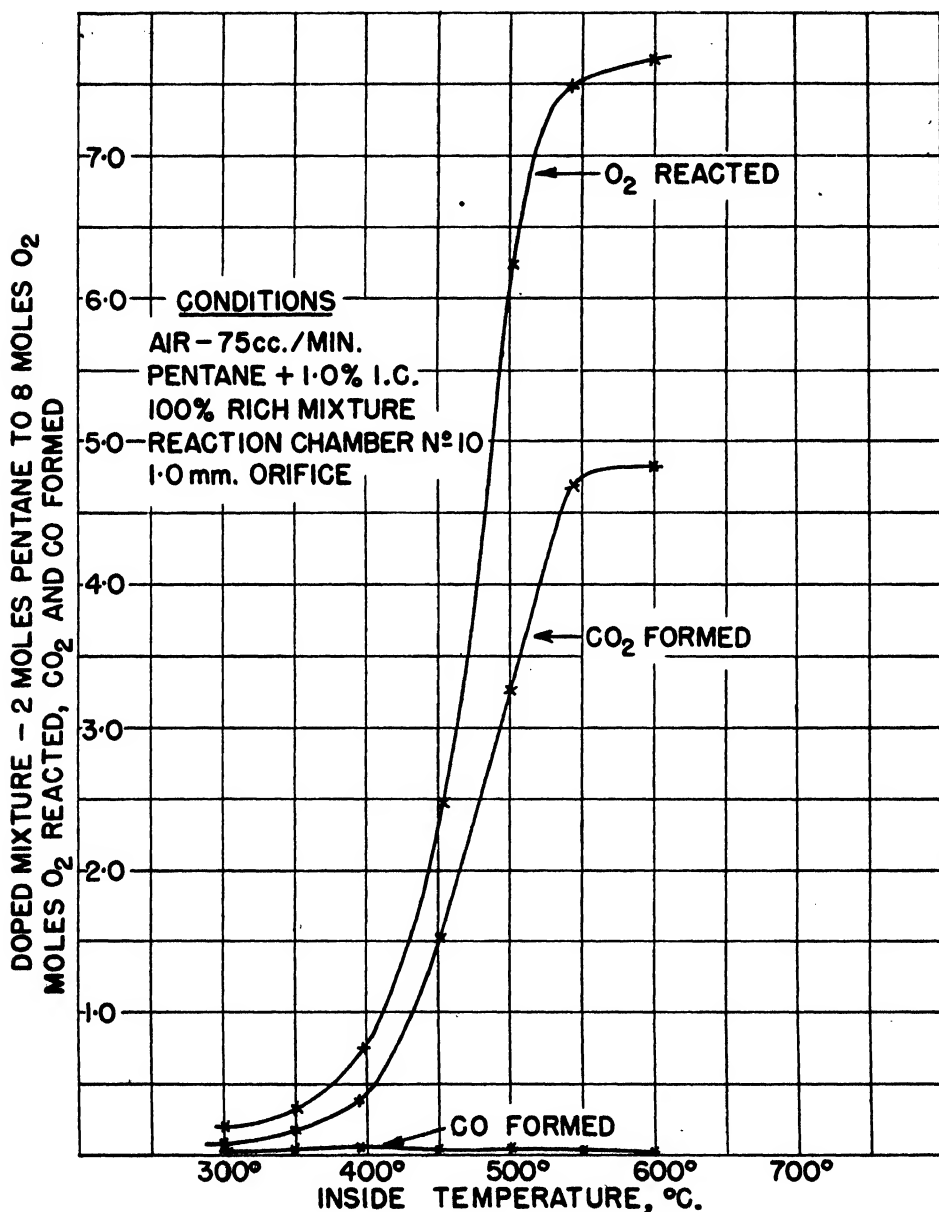


FIG. 5. Rates of formation of carbon oxides, 100% rich doped pentane-air mixture supplied at 75 cc. per min.

(3, pp. 130-131) it was shown that although aldehyde instead of final products was formed in reaction chamber No. 10 on converting the metal previously deposited on the active surface gradually to oxide, reaction velocity was less than when the surface was clean glass. On increasing the rate of mixture

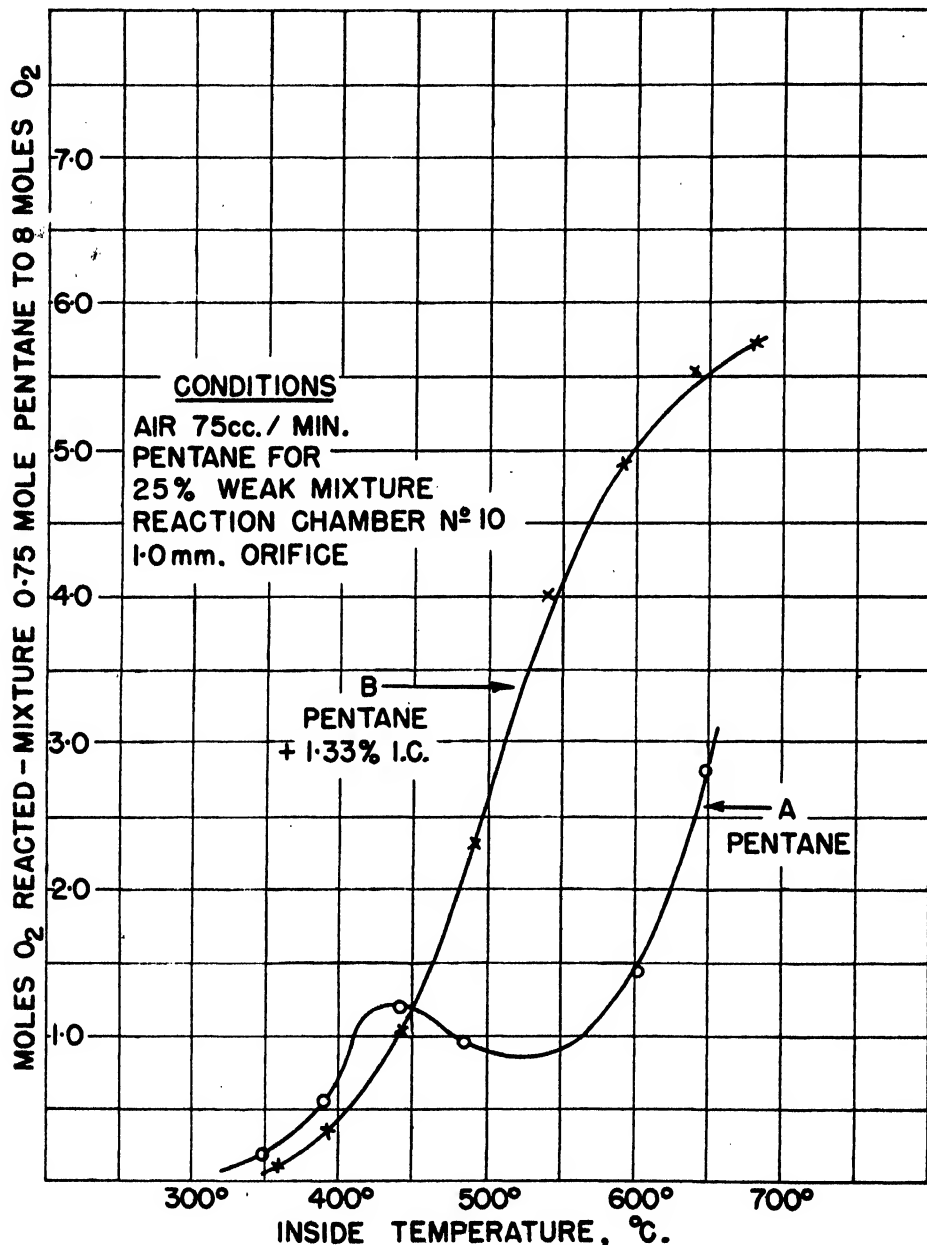


FIG. 6. Rates of oxygen reacted, 25% weak pentane-air mixture, with and without iron carbonyl, for flow configuration fixed by supplying the mixture at 75 cc. per min.

supply to 75 cc. per min. and thereby obtaining a deposit of metal on the active surface of the chamber, aldehyde is no longer obtained and reaction is to steam and carbon dioxide only, graph *B*, Fig. 2.

The experimental results, similarly to those given earlier (1, 2, 3), support the view that the low temperature oxidation of pentane and presumably

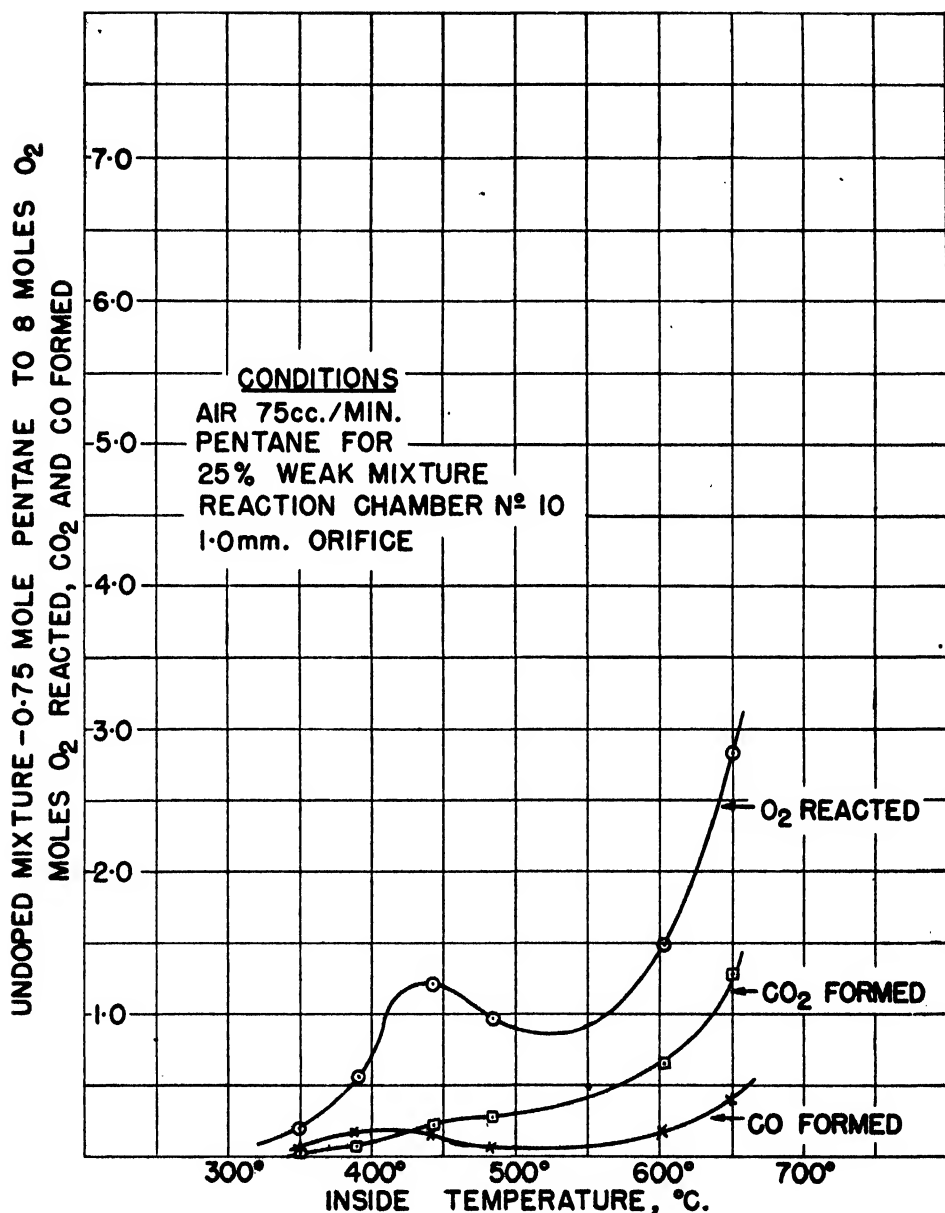


FIG. 7. Rates of formation of carbon oxides, 25% weak undoped pentane-air mixture supplied at 75 cc. per min.

similar hydrocarbons is a surface reaction; not one that can be explained by chain reaction theory. It is of interest that many attempts made accordingly have not led to any agreement in respect of the nature of the chain carriers or of the assumed unstable reaction products which are required to maintain the reaction (see review by Ubbelohde (5, pp. 2945-2947)).

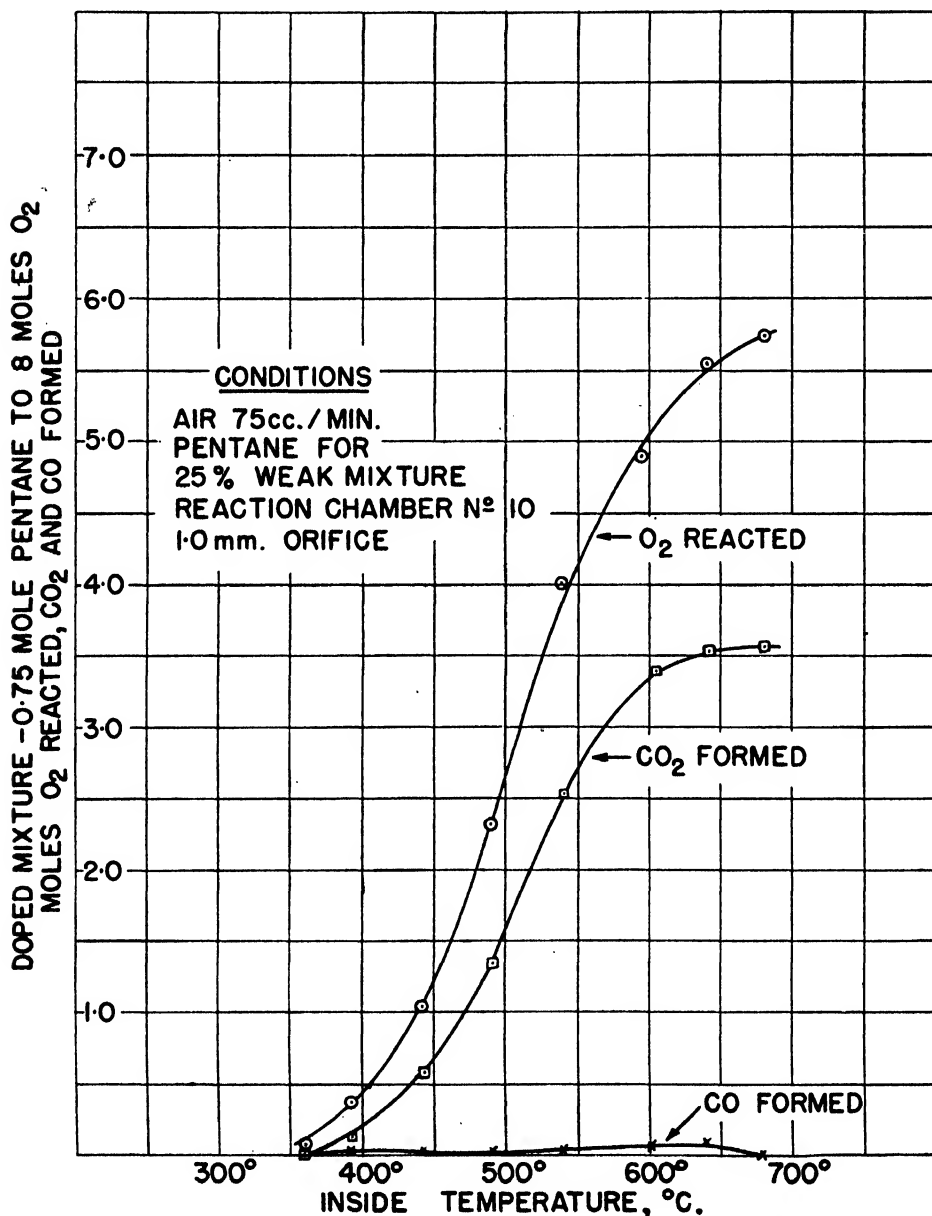


FIG. 8. Rates of formation of carbon oxides, 25% weak doped pentane-air mixture supplied at 75 cc. per min.

Mixture Strength and Reaction Velocity, Doped Pentane

Collected graphs showing rates of oxidation in weak, combining proportions and rich doped mixtures are given, Fig. 10. A remarkable increase in reaction velocity on increasing mixture strength is shown by the graphs. Thus,

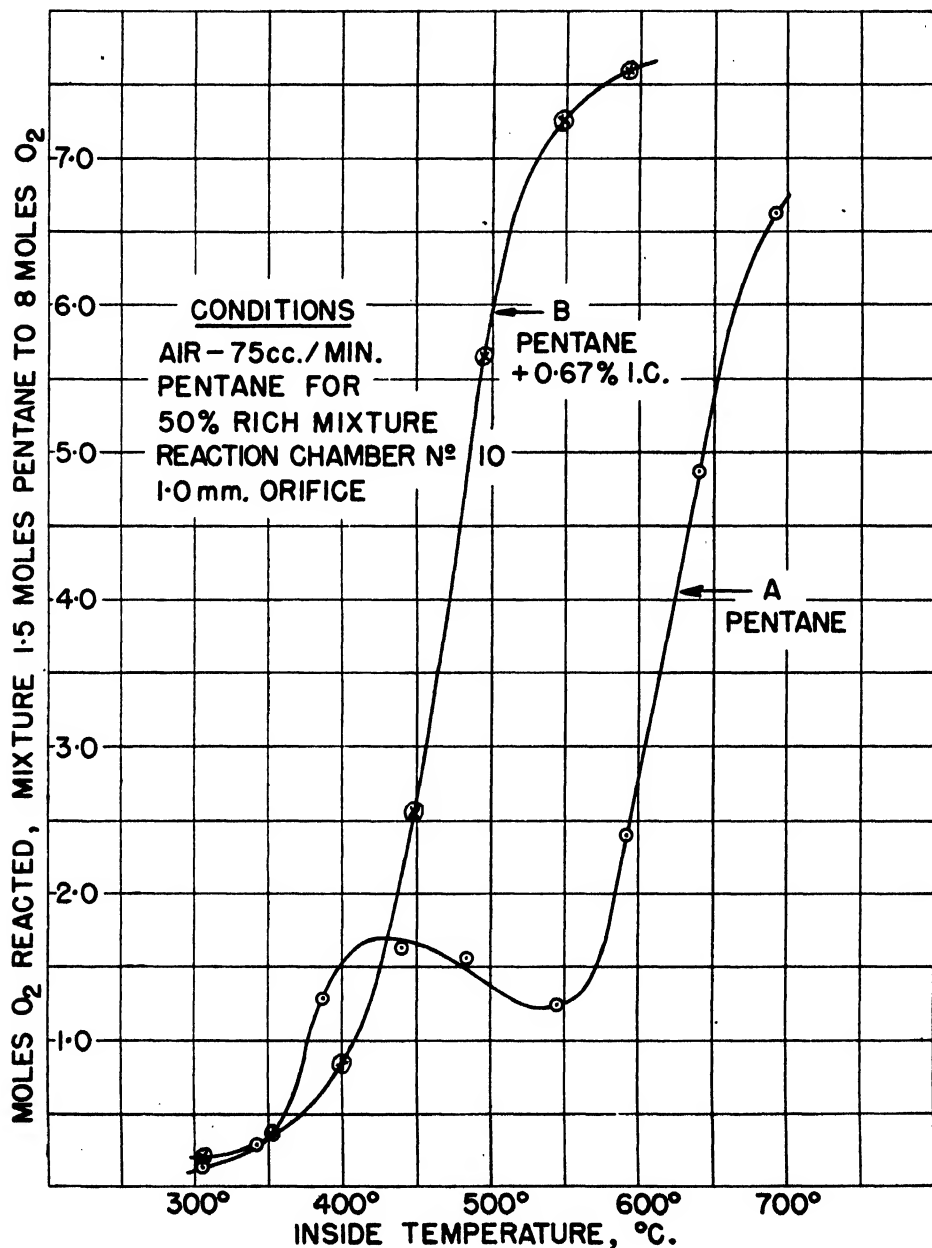


FIG. 9. Rates of oxygen reacted, 50% rich pentane-air mixture, with and without iron carbonyl for flow configuration fixed by supplying the mixture at 75 cc. per min.

substantially all the oxygen in the rich mixtures was reacted at 550° C. to form steam and carbon dioxide, graph 1, whereas in the 25% weak mixture about 5.8 moles only of oxygen out of the 8.0 moles available were reacted

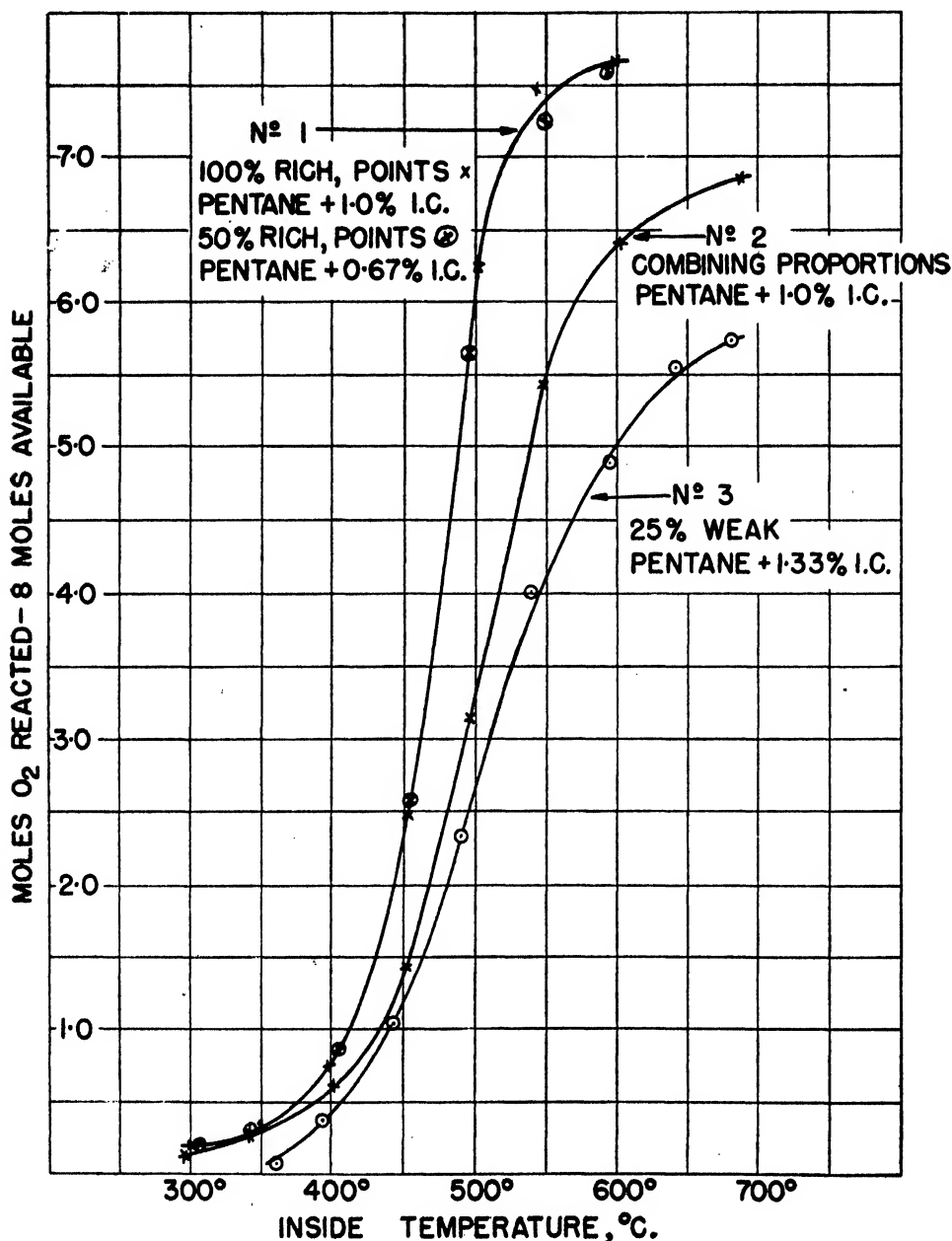


FIG. 10. Collected graphs showing that oxygen reacted for doped pentane-air mixtures reaches a limiting value, at all temperatures of reaction without explosion on increasing mixture strength and dope concentration.

even at the relatively high temperature of 690°C . Reaction velocities at low temperature are also of interest. It will be noted, Fig. 10, that reaction began at a measurable rate at about 360°C . in the weak mixture but was easily measurable at 300°C . in the richer mixtures.

Reaction velocities for a particular flow configuration reach limiting values at all temperatures of reaction on increasing mixture strength. Thus a single graph, 1, Fig. 10, can be drawn through the experimental points obtained for the 100% rich mixture containing pentane plus 1% iron carbonyl and the 50% rich mixture containing pentane plus 0.67% of the dope. Reaction in both cases was to final products only, the rate of formation of carbon monoxide being inappreciable. The consequence is that the excess pentane in both cases was not even partially oxidized and there was no visible evidence during the experiments of decomposition. It appears, therefore, that the oxidation reaction took possession of the surface, and in the circumstances there was little if any decomposition of the pentane vapor at the temperatures of the experiments. It may be, therefore, that the *decomposition* of pentane is a heterogeneous reaction at least at temperatures below 700°C .

Mixture Strength and Reaction Velocity, Undoped Pentane

The course of the reaction when pentane only is oxidized in reaction chamber No. 10 is characterized by the rate of formation of carbon monoxide for any mixture strength reaching a maximum within the temperature range 400° to 450°C . and again over the temperature range beginning at 600°C . The carbon monoxide over the low temperature range doubtless derives in large part from the oxidation of the aldehyde which is formed at a rate increasing with increase of mixture strength. Reaction velocity would not, therefore, be expected to reach a limiting value until the mixture contained pentane and oxygen in equimolecular proportions.

Reaction velocity at temperatures above 600°C . is also characterized by an increase in rate of formation of carbon monoxide as mixture strength increases, Figs. 5 and 7, but aldehyde does not appear in the products of the reaction. Velocity appears to approach a limiting value as mixture strength is increased, and the experimental results indicate that it might be attained by using mixtures more than 100% rich in pentane and obtaining equilibrium in respect of the reaction products, namely, steam and the carbon oxides.

Nature of the Oxidation Reaction

It has already been mentioned that in the experimental conditions, which are similar to those prevailing in an engine, the oxidation of pentane over the temperature range of aldehyde formation appears to be a heterogeneous reaction. The experiments also indicate that oxidation at high temperature is a reaction of the same sort. Thus the pentane vapor can be exposed to any temperature up to 700°C . while reaction proceeds with high velocity to reach a limiting value, without the occurrence of ignition or explosion. Such effects could not be obtained if the reaction were homogeneous.

Oxidation of the End Gas in an Engine as Affected by Mixture Strength

The temperature attained by the end gas varies with many conditions of engine operation but in usual circumstances temperatures are estimated to rise from about 670° to 880° C. as the compression ratio is increased from 4 to 10 : 1 if taken when combustion is 90% complete, Part IV (4, p. 233). The high temperature range of the experiments described in this part may be taken as from 600° to 650° C. although in one set of experiments nearly 700° C. was reached. Although the engine end gas temperatures are the higher, the time of exposure of the mixture in the engine is shorter than in the reaction chamber, so oxidation characteristics may be taken as similar to those found in the reaction chamber at lower temperatures. Undoped pentane being considered, relevant data taken from the *A* graphs of Figs. 2, 3, 6, and 9 are set out in Table I below.

TABLE I
MOLES OXYGEN REACTED (8 MOLES AVAILABLE) UNDOPED PENTANE

Temperature, ° C.	Mixture proportion, pentane-air			
	25% Weak	Correct	50% Rich	100% Rich
600	1.5	2.0	2.8	3.1
650	3.0	4.2	5.4	6.5
700	—	—	6.7	—

It will be seen by reference to the table that irrespective of mixture strength an increase in rate of oxygen reacted of approximately 100% is obtained on increasing the temperature from 600° to 650° C. A further effect of especial significance in respect of detonation in the engine is that the proportion of the available oxygen reacted also increases by approximately 100% over the range of mixture strength given in the table, at either 600° or 650° C.

Acknowledgments

The experimental work described in this paper is part only of that carried out in the Colloid Science Laboratory, Cambridge University, with the co-operation of Prof. E. K. Rideal and Dr. F. H. Garner and the assistance of Mr. R. R. Davidson, Emmanuel College.

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AN ULTRAVIOLET PHOTOMETER¹

By R. B. HARVEY²

Abstract

A photometer for use in the near ultraviolet has been designed and built with particular attention to simplicity, ruggedness, and reliability.

The construction of a photometer involves two problems—

1. The provision of a light source of the desired wave length and of constant intensity, and
2. The measurement of the change of property, usually intensity, of the light when it is passed through the substance to be investigated.

The provision of a constant light source of the correct wave length has been dealt with in several ways. Ballard and Thornton (1) used a 4 w. germicidal lamp, a large proportion of the radiation of which is of wave length 2537 Å. The germicidal lamp is fairly satisfactory as a source of 2537 Å as it emits little heat and it operates on 110 v. a.c. with standard accessories. Hanson (2) and Klotz (3) have used low wattage bulbs, but they introduced a constant voltage transformer and an inductance-capacitance network to stabilize the lamp. Silverman (5) wished to work at wave lengths slightly longer than 3000 Å and used an AH-4 lamp (100 w. mercury vapor) and a voltage and current stabilizing network similar to Hanson's. An argon bulb* has also been used to some advantage for work in the near ultraviolet. A sodium arc was used by McFarlan, Reddie, and Merrill (4) for vitamin A analyses at 3303 Å.

With the present instrument the measurement of change of light intensity was accomplished by means of a photocell, a direct current amplifier, and a milliammeter. The photocell** chosen was the RCA 929 with a maximum sensitivity in the region of 3800 Å. The amplifier is conventional. The photocell current flows through a 100 megohm grid resistor to cause a change in grid voltage; the variation of grid voltage is amplified and the resultant anode current change is read on a milliammeter. Ballard and Thornton (1) have a somewhat more elaborate balanced bridge system. Hanson (2), Klotz (3), and Silverman (5) used conventional single tube amplifiers.

The Photometer

In this photometer it was desired to have a machine powered entirely by the a.c. mains, rugged, simple to operate, and reliable over long periods of operation. An argon bulb (2½ w., 110 v. a.c.) was chosen as a light source

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² Major, Defence Research Board.

* Paper presented before the American Society of Biological Chemists, March 1938.

** Data on phototubes and circuits suitable to them are given in the RCA pamphlet "Phototubes." The basic design of the circuit in this paper was taken from page 10 of this pamphlet, 1940 ed.

because it emitted little heat and operated directly from the a-c. mains. The amplifier was built with a simple voltage stabilized high tension supply to render it less sensitive to plate supply voltage variations. The instrument was found to operate best with a Sola constant voltage transformer as a source of power.

This photometer was constructed in two parts. The light source - photo-cell unit was connected to the electrical measuring system by a length of shielded flexible cable which allowed considerable freedom of movement. It was desirable in this case to have the optical end of the instrument mobile, but there is no reason why the complete photometer cannot be built as an integral unit. The optical system consists of a light source ($2\frac{1}{2}$ w. argon glow lamp operating directly on the a-c. supply), a cell for the sample, and a photoelectric cell. The argon bulb was chosen as it gave a fairly good proportion of its radiation in the 3500 to 4000 Å region and because it caused no problem from emitted heat. The samples were contained in standardized test tubes such as are used for colorimetry. The photoelectric cell was a type 929 RCA sensitive in the region of 3800 Å. A diagram of this unit is shown in Fig. 1.

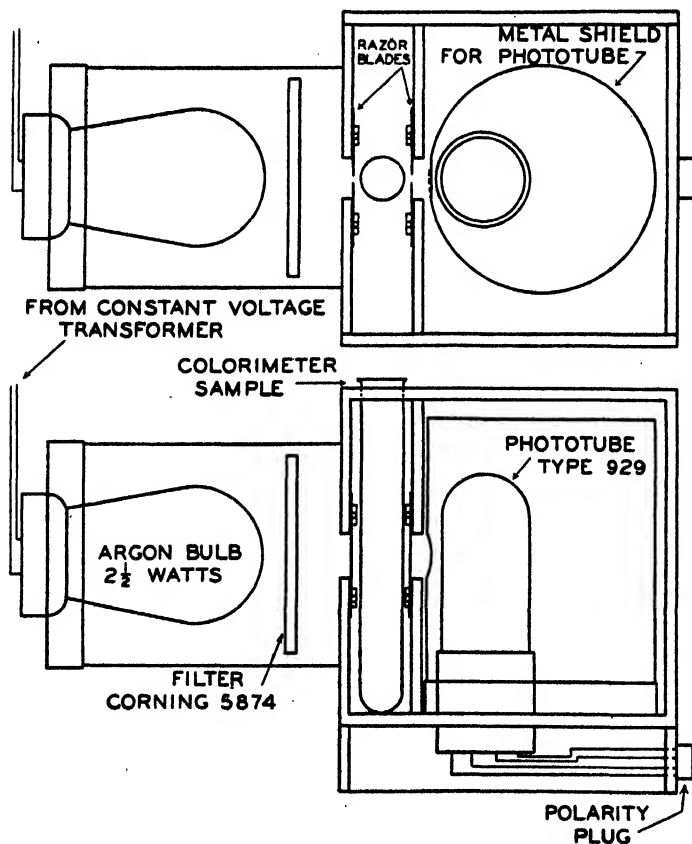


FIG. 1. Top and side views of mechanical arrangement of parts.

A two-wire shielded cable was used to connect the photoelectric cell of the optical unit to the amplifying unit. The latter unit, comprising the electrical parts, is shown in two diagrams for simplicity. Fig. 2, A, shows the photometer amplifier, Fig. 2, B, shows the power supply. The negative side of the high voltage is grounded and the + 75 v. and + 150 v. leads are connected to the amplifier as shown.

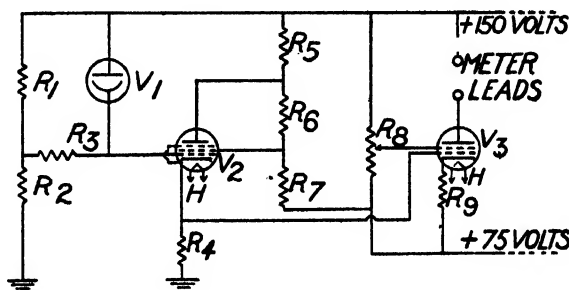


FIG. 2, A.

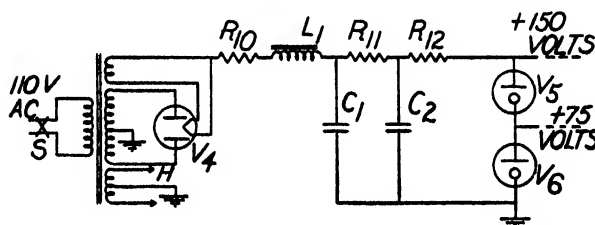


FIG. 2, B.

FIGS. 2, A, AND 2, B. *Power supply circuit and phototube amplifier circuit for photometer.*

R_1 , 500,000 ohms, $\frac{1}{2}$ w.

R_2 , 330,000 " $\frac{1}{2}$ w.

R_3 , 100 megohms precision (glass type).

R_4 , 500,000 ohms, 1 w.

R_5 , 30,000 " 1 "

R_6 , 20,000 " 1 "

R_7 , 30,000 " 1 "

R_8 , 10,000 " potentiometer.

R_9 , 2,000 " 1 w.

R_{10} , 5,000 " 20 "

R_{11} , 3,000 " 10 "

R_{12} , 2,000 " 10 "

C_1 and C_2 , 16 mf. 450 working volts.

L_1 , 10 h. 50 ma.

V_1 , 929 phototube (RCA type).

V_2 , 6SK7

V_3 , 6V6

V_4 , 5W4

V_5 and V_6 , VR-75 voltage regulator.

S , Double pole, single throw switch for 110 v. mains.

Meter, 0 - 1 ma.

Consider the amplifier shown in Fig. 2, A. Resistors R_1 and R_2 provide a potential across V_1 , the photoelectric tube. The values of R_1 , R_3 , and R_4 are chosen so that the grid potential of V_2 is near that of its cathode. Light falling on the phototube causes a current through the 100 megohm resistor R_3 (causing a positive voltage to appear at the grid end) and the potential so obtained is applied to the V_2 grid. The grid allows more current to flow in V_2 and makes the cathode end of R_4 more positive. This positive potential is applied to V_3 causing an increase of current in V_3 and, consequently, through the meter. The resistor system R_5 — R_7 inclusive provides screen and plate voltages for V_2 , and R_8 provides a variable screen potential for V_3 and allows

the meter reading to be varied or set at any desired figure. The positive voltages (i.e., + 75 and + 150 v.) are taken from voltage regulating tubes to increase stability.

In Fig. 2, *B*, is shown the power supply. A Hammond type 270B transformer supplies the heater and high tension voltages. Resistors R_{10} , R_{11} , and R_{12} are used to reduce the potentials across the voltage regulating tubes to a safe value.

Operation

Operation is extremely simple. The machine is turned on and allowed to warm up for 10 to 20 min. When the instrument is to be used for ultraviolet colorimetry it is found best to insert a blank and adjust the reading on the meter to full scale. The sample is substituted for the blank, and a second reading taken. From a standard curve the concentration of the sample may be estimated directly.

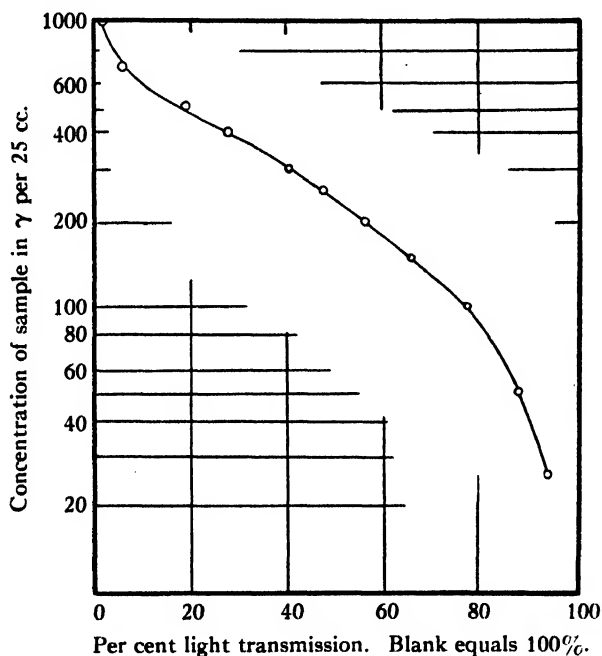


FIG. 3. Standard curve of concentration versus transmission for a heavy metal analysis.

In Fig. 3 is shown a typical standard curve for the photometer when it was used for the analysis of a heavy metal. This curve was obtained with a Sola constant voltage transformer delivering 124 v. as a power supply. The most useful fraction of the curve extends from 50 $\mu\text{gm.}$ per sample with transmission 88% of that of the blank to something about 700 $\mu\text{gm.}$ with transmission 7% of that of the blank, although this range may be extended somewhat at both ends with sacrifice of accuracy.

A few experiments were carried out to find the effect of a variation of supply voltage on the transmission readings for a given concentration. The supply voltages were obtained from a "Variac" fed by a constant voltage transformer and the voltage was read on an a-c. voltmeter to 0.1 v. These data are

TABLE I
THE EFFECT OF VARIATION OF SUPPLY VOLTAGE ON THE LIGHT
TRANSMISSION OF SEVERAL SAMPLES

Conc., $\mu\text{gm.}$	Supply volts						
	130	125	120	115	110	105	100
	Transmission readings						
10	98.5	98.5	98	98	98	98.5	98.5
25	97	96.5	95.5	95.5	95.5	96	97
50	90.5	90.5	89	88	88	90	—
150	75	70.5	65	69	71	73	—
250	54	48	47	51.5	54	61	62
500	21	20	19	24.2	32	38	—
1000	1	1	2	4.5	12	18	26
2000	0	0	0	1	4.5	11	17
3500	0	0	0	0.2	3	8	15

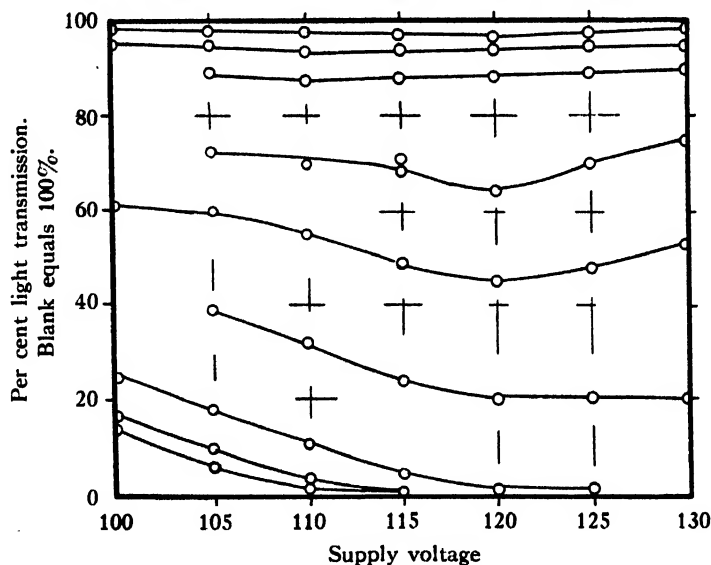


FIG. 4. Variation of light transmission with supply voltage.

given in Table I and plotted in Fig. 4. A suitable voltage at which to operate the instrument is probably about 120 to 125 v. as, on the whole, the transmission-voltage curves tend to be flattest in this region.

The best performance of the photometer has been obtained by feeding it with a constant voltage transformer. It has been found in operation that some care in measurements may be necessary in order to get the most from the photometer. Although the sample tubes used for these trials were the so-called colorimeter tubes, it was necessary to match the required number by comparison with one another from a stock of the tubes, as slight flaws were evident in the glass. Care was necessary to put the tube into the colorimeter always in the same way, as rotation of the glass caused fluctuations of the reading. It was found wise to eliminate gas bubbles from the tubes before measurement and each tube was inspected carefully every time it was inserted into the instrument. With these few precautions the reproducibility was as good as the accuracy of the meter readings.

These figures for the light transmission in this table were obtained by setting the blank to 100% transmission at the voltage chosen, measuring the percentage transmission of the sample and, immediately, reinserting the blank to ensure that its transmission remained constant at 100%.

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AN INK-WRITING CARDIOCHRONOGRAPH FOR THE STUDY OF THE ACTIVITY OF THE HUMAN AUTONOMIC NERVOUS SYSTEM¹

BY W. W. LOUCKS, S. S. KOSTASHUK, AND ALAN C. BURTON

Abstract

A study of the fluctuations of cardiac period from beat to beat gives information as to the activity of the vagus and sympathetic nerves which control heart rate. The instrument uses the electrocardiac voltages (Q.R.S. complex) between right arm and left leg, with the left arm grounded to the instrument. The out-of-phase voltages are amplified first by a differential amplifier, of high discrimination, then by a two stage pulse amplifier. The output is further amplified and distorted by a 'pulse-shaping' circuit to give a positive-going triggering impulse. This impulse, by 'striking' the thyatron of a 'sweep generator', causes the discharge of a condenser which has been slowly charging at a nearly constant rate. A recording milliammeter, of the ink-writing type, is connected to the condenser through a 'sweep amplifier' so that it draws a series of transverse lines on the record, the length of each being determined by the duration of the cardiac period before the next triggering impulse arrives. Over a long period of time, every successive cardiac period is recorded in a comparatively short record. Results have already shown the astonishing variability of the normal cardiac rhythm.

Introduction

A cardiachronograph (or cardi tachometer) is an instrument that records the instantaneous heart rate, or rather the period of each successive heart beat. The physician, when taking the pulse rate, usually counts the number of beats in 30 sec., or in an even shorter period, and so arrives at an average heart rate for the period of time of his observation. However, the heart rate, like all biological phenomena, has a wide fluctuation, and in the period of observation the "instantaneous rate" (the reciprocal of an individual heart period) may have varied widely from the average rate for the whole period.

The heart contains a "pace-maker," which initiates the rhythmic beats, but the rate is widely modified by two sets of nerves belonging to the autonomic nervous system, namely the cardiac accelerator nerves, part of the "sympathetic" nervous system, which speed the heart rate; and the vagus nerves of the "parasympathetic" system, which slow the heart. A continuous record of the spontaneous changes in heart rate, recorded by the cardiachronograph, will therefore give information as to the spontaneous activity of these nerves. Also, a cardiachronographic record of what happens to the heart rate when stimuli (emotional, drugs, etc.) are given to the subject, will give information as to the activity of the autonomic nervous system under these stimuli. With the increased interest in "psychosomatic medicine," which is concerned with phenomena in which the autonomic nervous system plays a very important role, the cardiachronograph becomes a very useful tool of research. With the growing interest in this field, it seems desirable that the apparatus should be described in some detail.

¹ Manuscript received May 31, 1948.

Contribution from the Departments of Physics and of Biophysics, University of Western Ontario, London, Ont.

Historical

The earliest reference known to us is the work of Boas (1) who constructed a "cardiotachometer," which, actuated by the electrocardiographic impulses, indicated on a counter (cyclometer) the number of heart beats in each minute. Independently, Fleisch (2) used the pulsation in volume of peripheral tissues with each heart beat to actuate a "Pulszeitschreiber." In this a pointer rose at a steady rate, drawing a vertical line on a smoked drum, until the cardiac pressure pulse interrupted its motion and it returned to zero, to start its upward motion again after a fixed short interval of time. Thus if the heart period were long, a tall vertical line would be drawn on the record, if the period were short, a short vertical line would be drawn.

The inherent difficulty with the method of Fleisch is due to the use of the peripheral change of volume of a limb with the heart beat to trip the mechanism, for during periods of constriction of the blood vessels, this will greatly decrease in amplitude. Also there is an appreciable lag in the time at which the pulse reaches the periphery, and this lag is not constant, because the "pulse wave velocity" changes with the state of tension of the blood vessels. Thus the changes in heart period would not be accurately recorded where vascular changes were also present. For this reason Whitehorn, Kaufman, and Thomas (4), and later White and Gildea (3) combined the use of the electrocardiographic impulse (the "Q.R.S. complex") to actuate the trigger mechanism with the "Zeitschreiber" principle of Fleisch (with some mechanical modifications).

A cardiotachometer on this principle, but utilizing photographic recording of the horizontal movement of a line of light from a mirror galvanometer (which executed the interrupted "sweeps") on vertically moving bromide paper, was developed by the Aero-Medical Research Unit of the Mayo Clinic, U.S.A.A.F., for use in experiments in acceleration. We are indebted to them for a circuit diagram of their arrangement. The instrument here described differs in design of circuits and in utilizing an ink-writing recording milliammeter. (Easterline-Angus). It is less expensive and more convenient to operate than photographic recording equipment.

General Description

This cardiotachometer consists of an amplifier to amplify the Q.R.S. complex of Lead II (right arm to left leg), a linear-sweep generator, counter circuits for providing calibration pulses, and a moving-paper ink-recorder.

The first stage of the pulse amplification consists of a differential amplifier. Fig. 2 shows a block diagram of the complete unit. Three electrodes are used on the subject. The left-arm connection is grounded. The right-arm and the left-leg electrodes are connected to the two inputs of the differential amplifier. The out-of-phase cardiac voltages which appear across the input of the amplifier are amplified and passed on to the next stage of pulse amplification. The in-phase voltages, due to stray pickup by the body, are rejected

by the amplifier. A balance control allows adjustment of the gain for each electrode so that the in-phase voltages can be cancelled out. An electric-eye indicator is used to give visual indication when the balancing is correct. (Figs. 1, 2, 3, and 4 give the scheme of circuits, the complete circuit diagrams, and mounting details.)

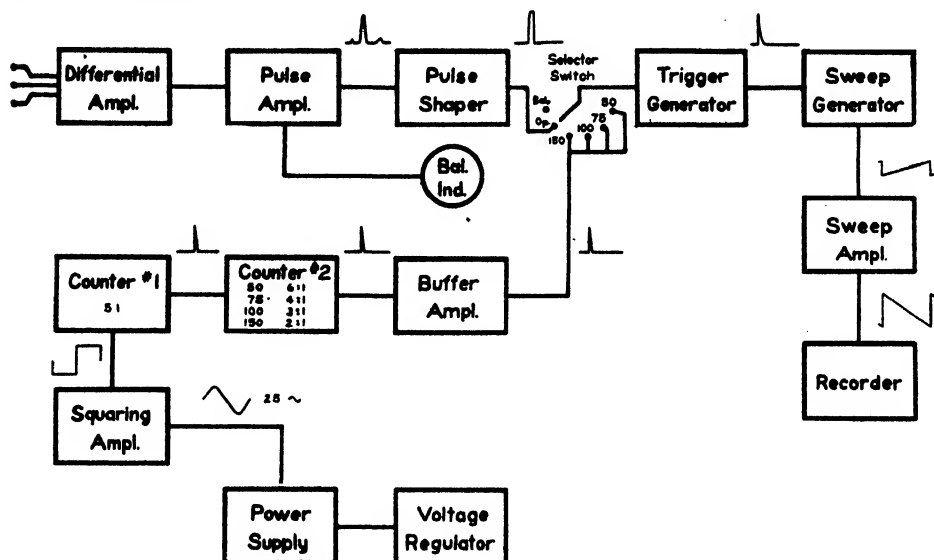


FIG. 1. *Cardiochronograph—Block diagram.*

The "pulse amplifier" provides two more stages of amplification. The second of these contains a gain control which permits adjustment for differences in cardiac voltage of individual subjects.

The voltage output from the pulse amplifier is fed into a "pulse shaper." Here the Q.R.S. complex of the cardiac potential is amplified further and distorted to give a sharp trigger pulse for the trigger generator. This consists of a thyratron which is normally extinguished. The arrival of a trigger pulse causes the tube to strike, thereby discharging the charged condenser in its plate circuit. In this manner a trigger pulse of constant amplitude and duration is produced coincident with each heart beat. This trigger pulse is used to control the action of the "sweep generator."

The sweep generator uses another thyratron to discharge a slowly charging sweep condenser at the instant a trigger pulse is received. Upon completion of the discharging of the condenser, the thyratron extinguishes, and the condenser again begins to charge, and is once again interrupted in its charging process by the succeeding pulse from the trigger generator, long before it reaches its full charge.

The series of saw-teeth of irregular amplitude as produced by the sweep generator is applied to the sweep amplifier. This stage is essentially a bridge circuit with a 5 ma. recording meter in the balance arm of the bridge. The

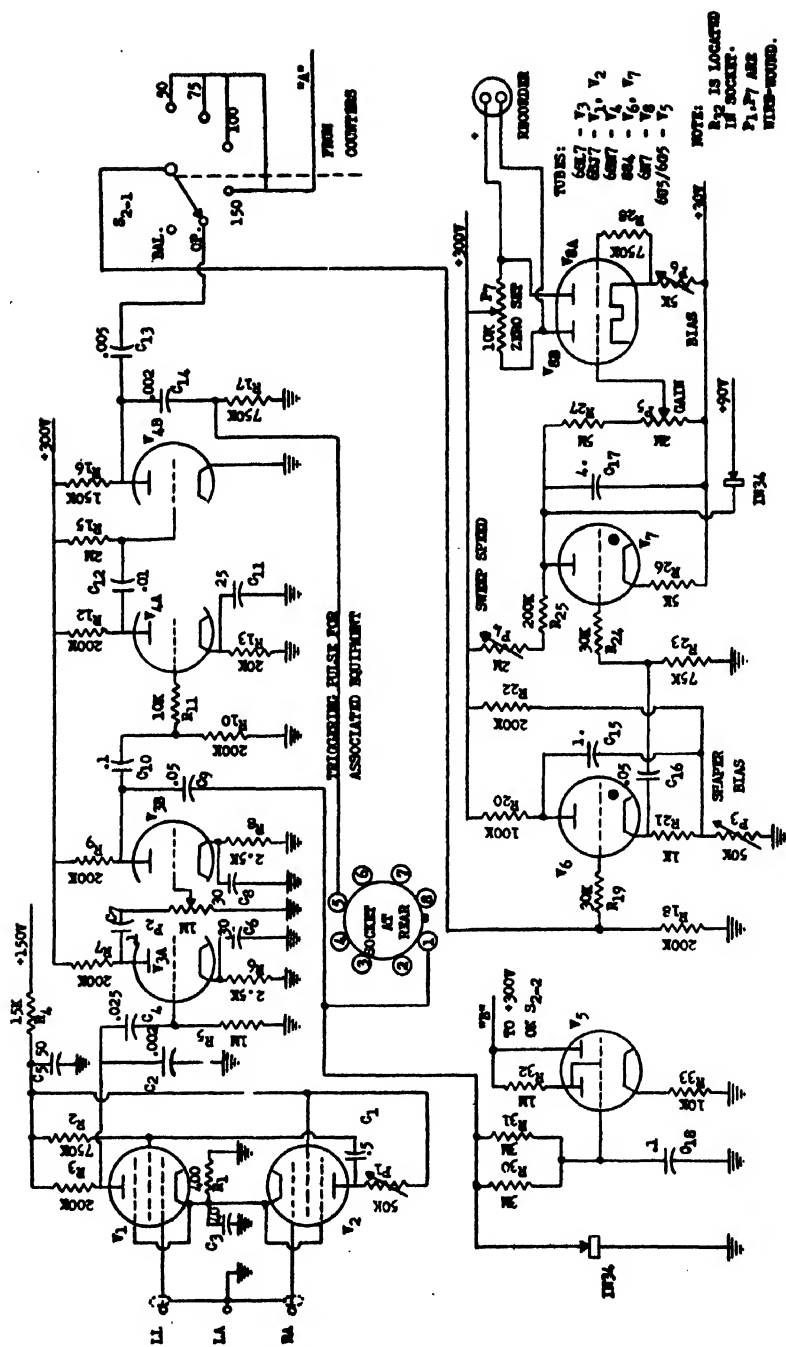


FIG. 2. Cardiochronograph—Amplifiers and sweep circuits.

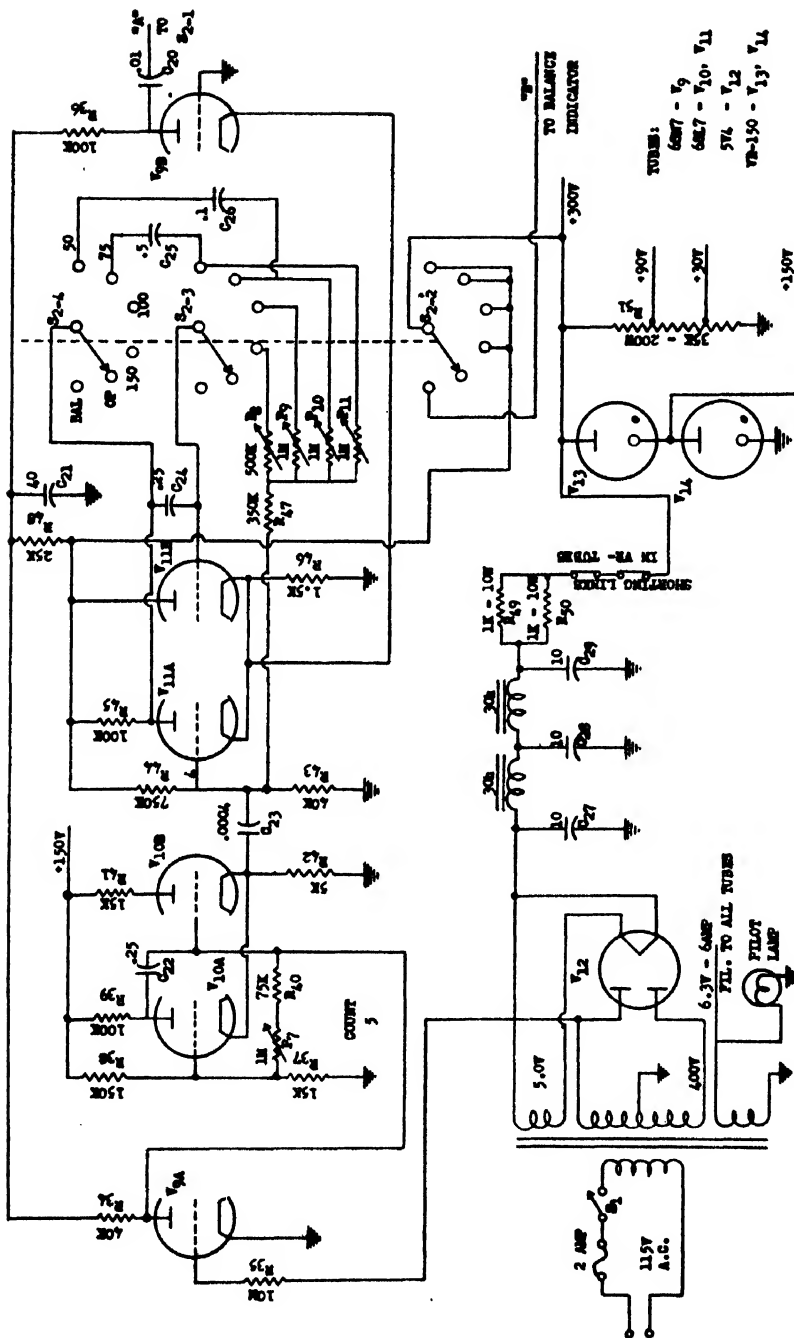


FIG. 3. Cardichronograph power supply and counters.

series of saw-teeth is recorded on a slowly moving strip of paper so that each saw-tooth appears as a spike.

Summarizing briefly, we find the recording arm moving from zero towards full deflection. A heart beat is received, and the arm is immediately sent back to zero from where it once again starts sweeping towards full deflection. Another pulse sends it back to zero, and so forth. The length of the traces on the paper is therefore a measure of the period of successive heart beats (see Fig. 5).

Calibration circuits are provided for a convenient indication of the length of trace corresponding to different heart rates. Pulses at rates of 50, 75, 100, and 150 per min. are produced by the counters of the calibration circuits. The line frequency, which in this case happens to be 25 cycles per sec., is used to initiate the counters.

The power supply provides regulated d.c. at 300 and 150 v. for the operation of the circuits of the cardiochronograph.

Circuit Detail

Differential Amplifier

This consists of two type 6SJ7 pentodes. V_1 is a normal amplifier tube whose screen grid is coupled to the anode V_2 . The balance control P_1 , is adjusted so that the gain of V_2 plus the screen grid to plate gain of V_1 is equal to the control grid to plate gain of V_1 . Thus if equal in-phase voltages are impressed on the control grids of V_1 and V_2 , the effect on the output of V_1 is negligible, since the voltage applied to the screen of V_1 just neutralizes the effect of the voltage applied to its control grid. In this way, a rejection ratio of better than 500 to 1 is realized, and no screening of the subject from stray pickup is necessary. Because of the high amplification necessary in this equipment, it is advisable to insulate the sockets of these two tubes with soft rubber, thereby minimizing the electrical effects produced by mechanical vibration.

Pulse Amplifier

This consists of the two halves of a 6SL7, a high-gain double triode. A gain control, P_2 , is provided in the input of the second half of this tube. The total gain of the amplifier circuits is approximately 100,000 maximum.

Pulse Shaper

A type 6SN7 medium-gain double triode is used in the pulse-shaper stage. Its purpose is to amplify and distort the Q.R.S. complex so that a steep-fronted trigger pulse is obtained (see Fig. 1). V_{4a} is normally biased to beyond cutoff. This insures that the P and T waves of the cardiac potentials, as well as any minor muscle action potentials, do not pass through the amplifier. Furthermore, the top of the Q.R.S. complex is clipped off owing to grid current flowing. Thus a fairly broad, negative-going square wave is passed into V_{4b} . This second triode, which on no-signal conducts at saturation, inverts and peaks the square wave. The resulting positive-going trigger pulse is brought over to the trigger generator at the "operate" position of the selector switch.

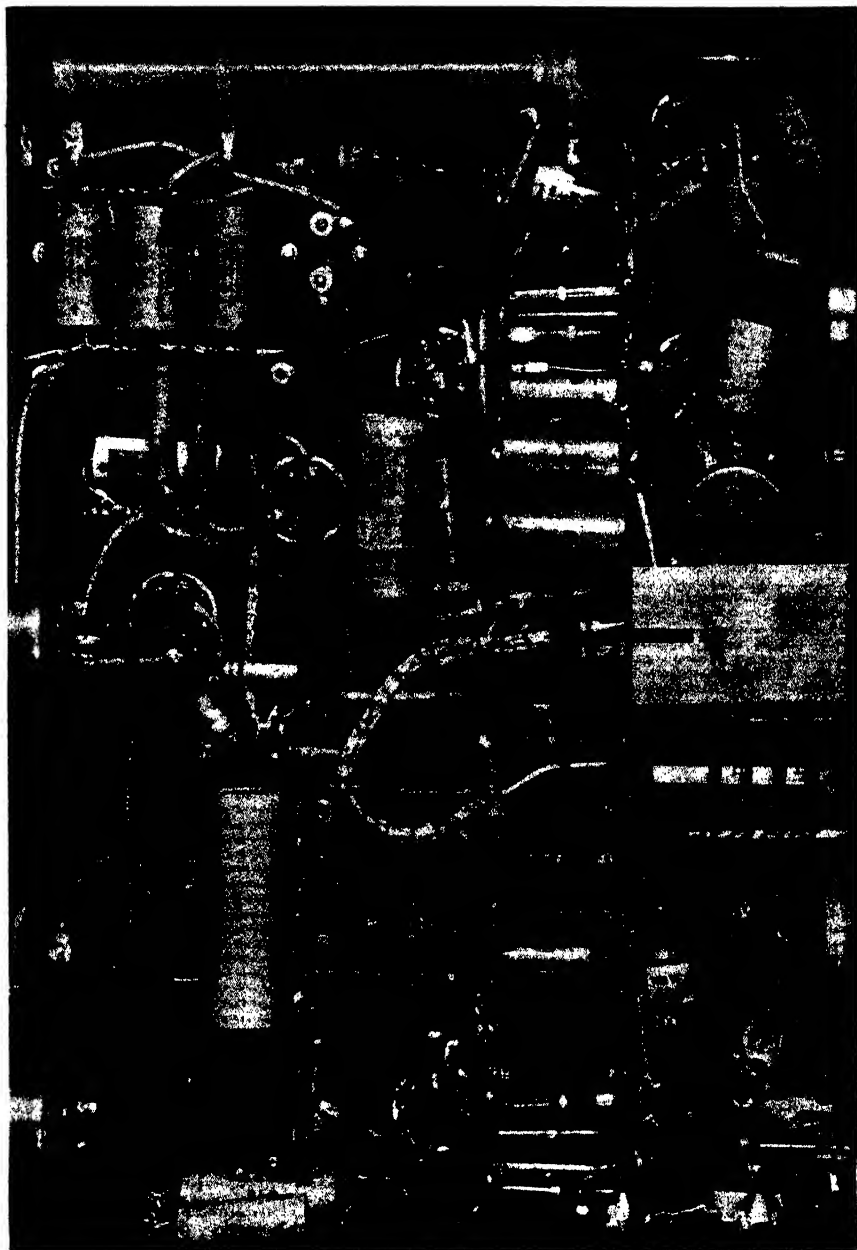


FIG. 4. Bottom view of cardiochronograph.

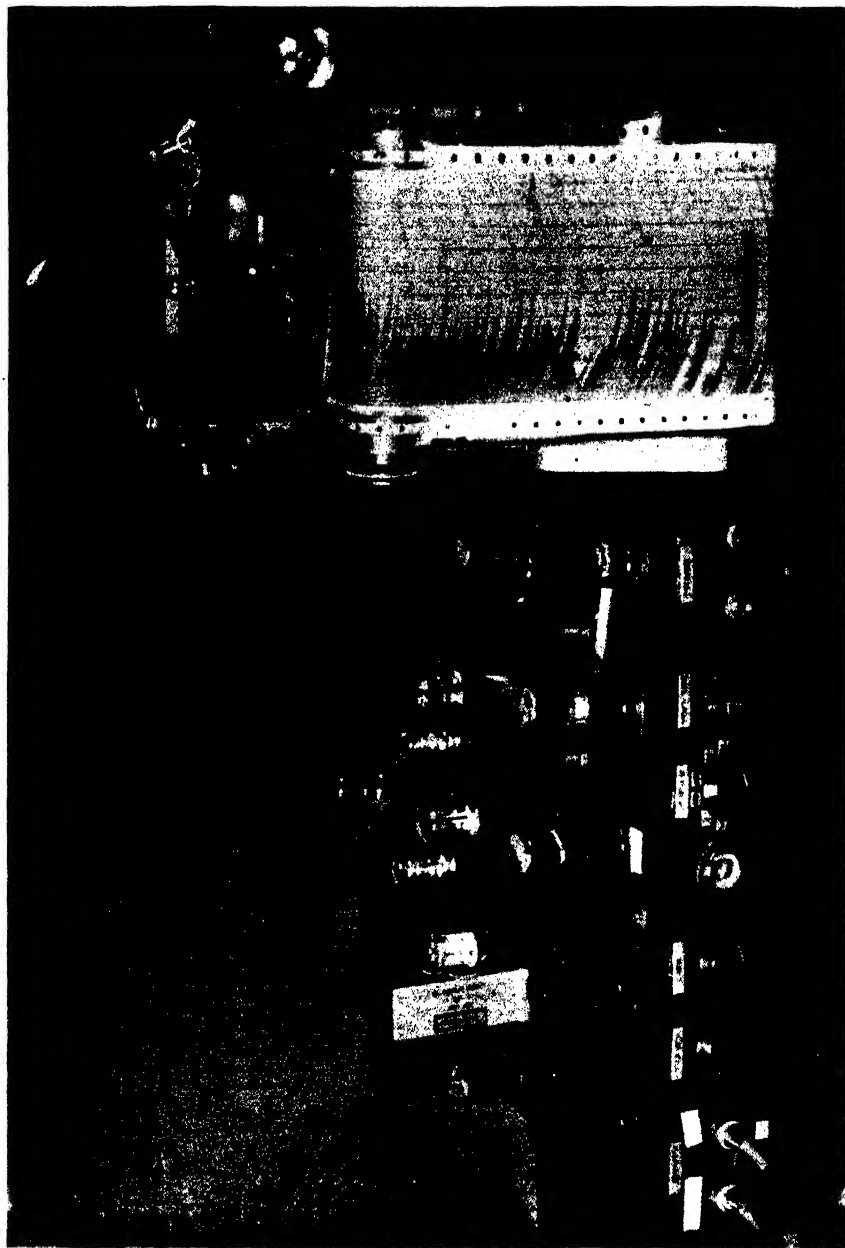


FIG. 5. Complete apparatus (with covers removed).

Balance Indicator

The output of the pulse amplifier is at all times fed into a type 1N34 crystal rectifier, associated with a "magic-eye" indicator tube, V_5 . This crystal rectifies any a-c. component in the amplifier output and the resultant d.c., whose magnitude is proportional to the a-c. in-phase and unwanted component, is applied to the control grid of V_5 .

With zero voltage on the grid, the bias has been set by R_{33} so that the eye is almost closed. Application of positive d-c. voltage from the crystal, via the smoothing filter, causes the eye to open. Thus, if the balance control, P_1 , is properly adjusted for no in-phase voltages leaving the differential amplifier, the eye will be at minimum opening. The H.T. for V_5 is switched on by section 2 of the selector switch when in the balance position only. Thus the eye is illuminated only in this position. (Experience with the instrument has led us to prefer that the balance control should be omitted from the front panel and "pre-set," while the "magic-eye" would be retained to indicate the magnitude of the cardiac impulses coming through.)

Trigger Generator

This circuit employs a type 884 gas triode or thyratron, V_6 . For every trigger pulse received by this tube, a pulse of constant amplitude and shape is delivered at the cathode output owing to the discharging of C_{15} through the tube. This trigger pulse retains its constancy regardless of the nature of the triggering pulse applied to the grid of the tube. A pre-set "shaper bias" control, P_3 , is used in the cathode circuit of this tube to permit accurate adjustment of the bias.

Sweep Generator

The sweep generator, V_7 , also uses an 884 thyratron. By means of an adjustable slider on the voltage divider of the power supply, this tube is biased so that it remains extinguished with no signal on the grid. In this case, 30 v. is a satisfactory bias. The trigger pulse causes the thyratron to 'strike' and discharge C_{17} in the plate circuit. As soon as the plate-to-cathode potential drops to the extinction value (about 18 v.), V_7 ceases to conduct and C_{17} begins to charge exponentially through the plate-load resistors. The rate of charge is controlled by P_4 , the pre-set sweep-speed control. The charging condenser voltage is applied across R_{27} and the gain control, P_5 . From the latter control, a reduced saw-tooth voltage is applied to the sweep amplifier.

When no trigger pulses are received at the grid of the sweep generator, the condenser C_{17} would charge up to 270 v. Since the sweep amplifier is directly coupled, a voltage of such magnitude would overload it and cause the needle of the recorder to remain hard over at maximum deflection. To prevent this, a 1N34 crystal unit is placed in the plate circuit of V_7 to act as a voltage limiter. The negative end of the crystal is attached to a slider on the voltage divider bleeder. The latter is adjusted so that the recorder needle will rest at slightly under maximum deflection when no trigger pulse is applied to the

sweep generator (for example, when the selector switch is in the balance position). This limiting voltage is approximately 90 v.

Sweep Amplifier

The sweep amplifier circuit is actually a bridge circuit wherein each triode section of a 6N7 forms a branch of the bridge. The two remaining branches are made up of the adjustable plate resistors, formed by P_7 , the zero-set control. This control is located on the front panel of the instrument and is used to set the "75 pulses per minute" calibration sweeps coincident with the center ruling on the recording tape.

The pre-set bias control, P_6 , adjusts the operating point on the "grid base" of the triode V_{8a} which serves as the "active" branch of the bridge network. It thus serves as a linearity control for the sweep.

Ink-recorder

A 0-5 ma. Easterline-Angus ink-writing recorder is used (Fig. 5). This meter had to be modified for rapid writing, because the instrument, as designed, is overdamped. This is because the moving coil is wound on a copper former made of a strip whose ends are soldered together under the winding. This junction was carefully opened without disturbing the coil, and transformer fishcloth was inserted between the ends, insulating them from one another. The assembly was glued back together with radio cement. The required amount of damping was found to exist when two $\frac{3}{4}$ in. lengths of No. 18 B & S copper wire, in parallel, were soldered across the junction.

Another modification of a minor nature consisted of attaching a solid rubber covered metal stop at the zero end of the recording needle in place of the flexible wire stop used on the instrument. This prevents excessive bounce on the needle fly-back. It was also found best to adjust the zero set of the instrument so that the needle rests at approximately mid-scale when no current is passed through it.

When operating, the recorder is made to travel at the "rapid feed" position, and the timing lever is adjusted for a feed of one transverse division of the recording paper per half minute.

A manometric recorder to write a record (on the same moving paper) of the depth and rate of respiration has also been mounted in the instrument.

Calibrator Circuits

These circuits consist of a squaring amplifier, two counters, and a buffer amplifier. Refer to the block diagram, Fig. 1.

Squaring Amplifier

One-half of a 6SN7, V_{8a} , is used to square a 400 v. (R.M.S.) sine wave, taken from the secondary winding of the 25 cycle power transformer. The resultant square-wave at the anode is differentiated in the coupling network, and the positive-going peak is used to trigger the first counter.

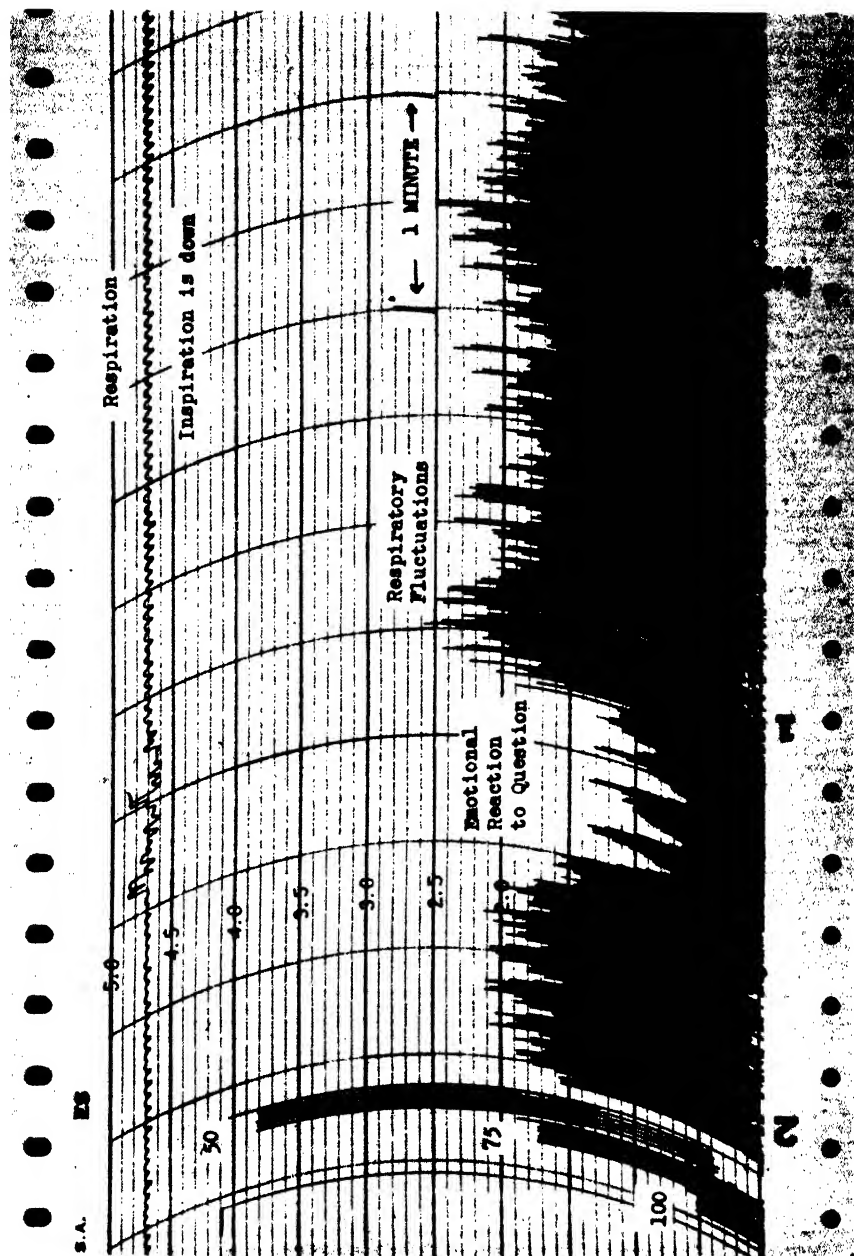


FIG. 6. Record of normal subject, to be read from right to left. The calibration is shown on the extreme left-hand side.

First Counter

The first counter, V_{10} , is a cathode-coupled multivibrator using both triodes of a 6SL7. Its natural frequency is approximately two cycles per second. By adjusting P_7 , every fifth peak from the squaring amplifier is made to trigger the multivibrator before its natural time, thereby setting its frequency at 5 cycles per sec., or 300 cycles per min.

The cathode of this multivibrator is coupled to the second counter through a differentiating CR.

Second Counter

The second counter is also a cathode-coupled multivibrator. Two sections of the selector switch permit a change-of coupling time constants to provide frequency rates of 50, 75, 100, and 150 cycles per min. (that is, counts of 6, 4, 3, and 2 respectively). The cathode circuit of this multivibrator is also the cathode circuit of the buffer amplifier, which is of the grounded-grid variety. The positive-going output is applied to the trigger generator at the "calibrate" positions of the selector switch, section 1.

Power Supply

The power supply uses a transformer supplying 800 v., center-tapped, for rectification. The d-c. output is regulated against line voltage surges by means of a pair of VR-150's, in series. A wire-wound bleeder with adjustable taps provides the necessary voltages for the sweep circuits, as described earlier.

The transformer also contains a secondary winding supplying 6.3 v. at 6 amp. for heater current.

Action of the selector switch supplies 300 v. d.c. to the "magic-eye" in the "balance" position, and to the counter circuits in the "calibrate" positions. These circuits are left without plate supply voltages in the "operate" position.

Results with the Instrument

The cardiograph has been in operation in research on the activity of the autonomic nervous system at the Medical School, University of Western Ontario, since February, 1947. This paper is not the place for any full account of results. A record of the heart rate and respiration of a normal subject, after lying quietly for 10 min., is shown in Fig. 6. It reveals, first, the unexpected degree of variability of heart period from beat to beat that is normally present. Such a variability would be quite unsuspected were it not for the cardiograph. In addition, rhythmic changes correlated with the respiration, and other cardiac accelerations and slowings not so related, are seen. The pattern of these changes is giving valuable information as to the activity of the nerves to which they are due. A simultaneous ink-writer record of the activity of the sweat glands, obtained by amplification of the bioelectric potential changes that occur, gives additional information. Details of this amplifier (the Electrical Sudograph) will be given in a separate paper.

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AN OMNIDIRECTIONAL, VERTICALLY POLARIZED, FOUR ELEMENT ANTENNA ARRAY¹

By R. S. RETTIE²

Abstract

An omnidirectional, vertically polarized antenna was required for use in the ground installations of the Airborne Distance Indicator program of the National Research Council. This antenna was to be mounted on the center tower of the Radio Range Beacons of the Department of Transport, and it was hoped that a certain amount of gain over a quarter-wave rod antenna could be realized. This paper describes an array of four elements stacked vertically, each element being a half-wave radiator in the form of a cylinder surrounding a mounting pipe. A gain of about four decibels over a half-wave dipole is obtained in a rugged and relatively simple form. Operation is possible over a 10% frequency band, centered on 223 Mc. per sec. It is suggested that similar antennas may find a wide field of application in the VHF band.

The Required Antenna

In many forms of radio communication, the antenna is designed to give nondirectional coverage in the horizontal plane together with the highest possible field strength on the horizon. This is a general problem in broadcasting and in mobile services on all wave lengths. On long and medium wave lengths such performance is obtained by the use of high towers and special current distributions. On shorter wave lengths it becomes practical to stack several radiators one above another. Such radiators are usually omnidirectional and are fed in such a way that their fields reinforce on the horizon and cancel at high angles. Such antenna arrays are typified by the turnstile antennas of G. H. Brown, in both horizontally and vertically polarized forms (1).

In the Airborne Distance Indicator program of the National Research Council of Canada, a ground antenna was needed which would be vertically polarized and omnidirectional, have a useful gain over a quarter-wave rod and ground plane antenna, and be capable of simultaneous operation on two frequencies in the band 215 to 230 Mc. per sec. It was desired to mount this antenna on top of the 125-ft. central tower of the Canadian Department of Transport Radio Range Beacons, and, as a result, it had to be self-supporting, robust, and if possible, totally enclosed in a weatherproof sheath. An over-all length of 10 to 12 ft. (about two wave lengths) was indicated as a useful size. Thus the problem was to design a group of four half-wave dipoles, or two full-wave dipoles arranged in line vertically. Such an antenna would give a gain of the order of 4 db. over a half-wave dipole, and somewhat more over a quarter-wave rod and a small ground plane.

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Possible Arrangements

The dipoles of such an array can be arranged either in series or in parallel. In the series form, usually called a collinear array, the antenna is fed at one end, and each element transfers power to the next through a phase-reversing section. This method was rejected because phase errors in these reversing sections are cumulative at other than the design frequency, and a severe limitation of the operating band results. In addition, such sectionalized antennas tend to be structurally weak.

In the parallel method of feeding, it is necessary to run the feed lines and a mounting pipe past some of the radiating elements. If this is done externally, serious interference with the radiators results unless the distance between the feed line and the radiators is large (at least one-half wave length); or unless a symmetrical arrangement of several radiators replaces the usual single radiator (1)—both clumsy and weak solutions of the problem. A natural development is to place the mounting pipe inside rather large radiators and to have the feed line inside the mounting pipe. Unwanted currents on the pipe cause no undesired directive effects in the horizontal plane, and the effect of these currents on the vertical directive characteristics and on the antenna impedance can be reduced by suitable methods of impeding their flow. Such antennas had been constructed previously at a wave length of 10 cm. using very fat dipole cylinders of radius about one-eighth wave length greater than that of the mounting pipe (3).

The Selected Design

It was decided to investigate the properties of an antenna similar to this last type, but having dipoles only slightly larger than the mounting pipe, the fact that this closer spacing would increase the currents induced on the mounting pipe being accepted. The effects of these currents are greatest near the ends of the pipe, especially the lower end where the terminating conditions are difficult to control. At the top end, the mounting pipe can be cut off at that distance found to be most useful in reducing the effects. A method of control at the bottom is to place a high impedance in the path of such currents. A quarter-wave choke, concentric with the mounting pipe, is very suitable for the purpose and its position is easily determined experimentally. The top of the antenna, as well as the bottom, can be fitted with such a choke, to provide flexibility in mounting other antennas, lighting fixtures, etc., above this antenna.

In the proposed antenna the radiators are four cylinders of sheet brass mounted on bakelite disks. The quarter-wave chokes are similar, but would have a metal disk short-circuited to the pipe at their remote ends. It appeared preferable to connect the radiators as full wave dipoles in order to simplify the feed arrangement and the matching problem. Two full wave dipoles in parallel would give an impedance of the order of 100 ohms (for the anticipated length-to-diameter ratio), while four half-wave dipoles in parallel would give

perhaps 20 ohms. The intended use of a shielded, balanced, two wire line inside the mounting pipe favored the use of high impedances.

In order to realize a pure resistance load, the radiators were made somewhat shorter than a half-wave long, and, with the feed points a full wave apart, there are consequently large gaps between the radiators. The actual spacings were made larger at the ends of the dipoles than at the feed points, since short and direct connections at the feed points were considered more important than equal radiator spacing.

Space was allowed in the base of the antenna for a balance-to-unbalance coupler (2) between the main feeder of flexible concentric cable and the more convenient balanced two wire line inside the antenna itself. Two methods of connecting the dipoles were available. The lower dipole could be tapped off the line running to the upper, although this would introduce certain variations of phase with frequency which might be objectionable in very wide-band operation. The alternative, with some extra complication, would be to run equal length feeders to the two dipoles from a branch point midway between them, the dipoles thus being kept in phase for all frequencies. The latter method was considered unnecessarily complex for an experimental antenna as described below.

Such an antenna can be totally enclosed in a plastic sheath and would then, in this example, resemble a pole 12 ft. long and $4\frac{1}{2}$ in. in diameter. If desired, a heater can be placed below the lower choke and a stream of warm air passed through holes in the various disks in order to reduce icing troubles.

The Experimental Antenna

An antenna was designed for a mean frequency of 223 Mc. per sec., the general plan outlined above (see Fig. 1) being followed. The mounting pipe was steel, $2\frac{1}{2}$ in. in diameter and 12 ft., 9 in. long. With a $\frac{1}{4}$ in. wall thickness, it formed an exceedingly strong structure. The radiators and chokes were cylinders of sheet brass, 22 in. and $13\frac{1}{2}$ in. long, respectively, and each 4 in. in diameter. The radiators were spaced $\frac{7}{8}$ in. apart at the dipole feed points, and 8 in. apart between the dipoles. The chokes were spaced $8\frac{1}{2}$ in. from the dipoles, as determined experimentally.

Each dipole was connected by $\frac{1}{2}$ in. diameter brass rods, $1\frac{1}{2}$ in. long, to a balanced transmission line of characteristic impedance equal to 185 ohms. Just below the feed point of the lower dipole, the line impedance changed from 185 to 96 ohms, and a quarter-wave transformer of 73 ohms impedance in the correct position served to match the two impedances. The balance-to-unbalance coupler at the base of the antenna consisted of a shielded parallel-conductor, quarter-wave stub, with the concentric feed line running inside one arm. At the same time this coupler incorporated a transformer to match the 96 ohm, two conductor line to the 50 ohm concentric feed line. Fig. 1 is a schematic drawing.

The Experimental Results

In order to investigate the free space vertical radiation pattern, the antenna was placed on its side and rotated in the horizontal plane. When the chokes

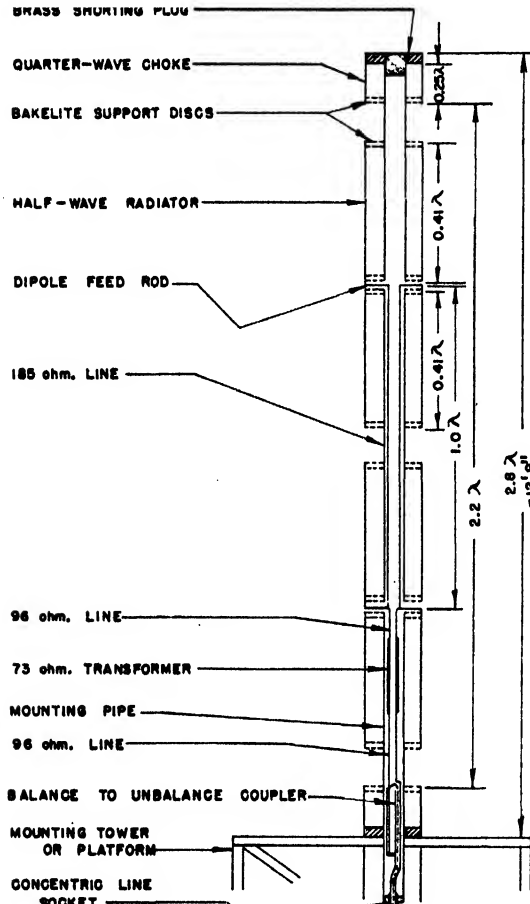


FIG. 1. The schematic diagram of the experimental antenna.

had been positioned for minimum side lobes the results shown in Fig. 2 were obtained at 223 Mc. per sec. Included for comparison in Fig. 2 is part of a theoretical pattern for four half-wave dipoles, spaced equally at half-wave distances, and fed in the same phase and amplitude. The larger side lobes in the experimental case are due to unwanted current still present, but are unimportant in the present application except for a minor decrease in gain. The true horizontal pattern is circular and thus the free space pattern is disk-shaped. The true vertical pattern should include the effect of ground reflection, but, owing to the high elevation of this antenna, the lobe structure

is fine, and in practice is not noticeable. The effect of the ground is then merely to cut off the radiation at angles below and very near to the radio horizon.

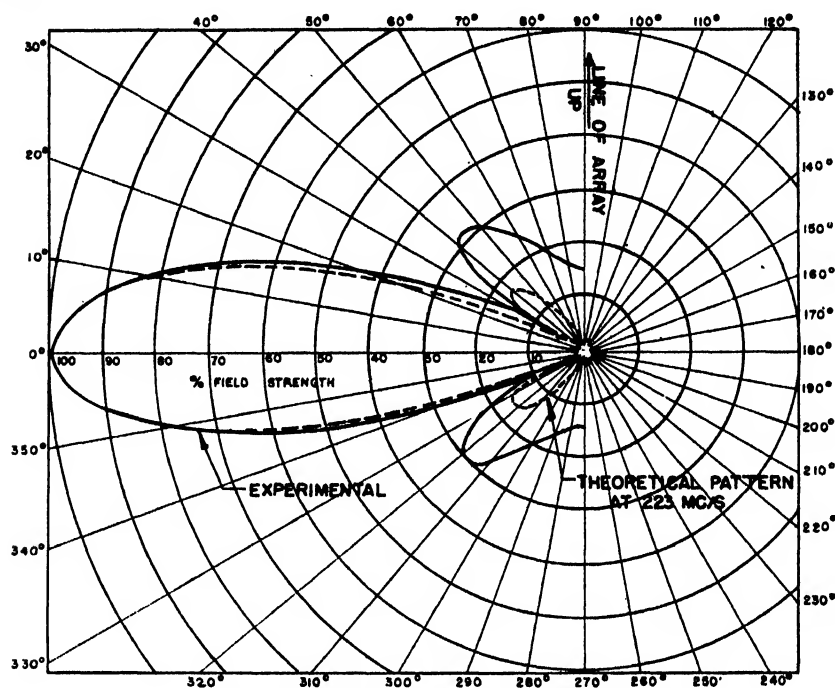


FIG. 2. The free-space vertical radiation pattern at 223 Mc. per sec.

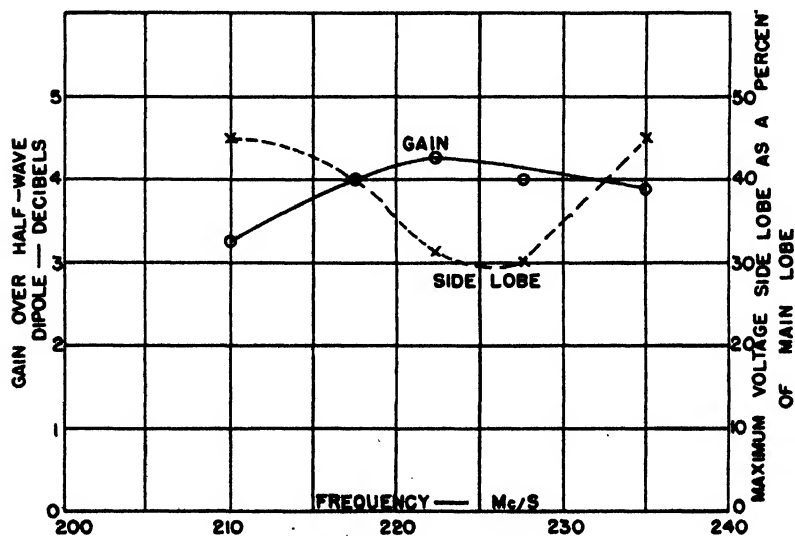


FIG. 3. The antenna gain and the maximum amplitude of side lobes plotted against frequency.

The gain of the antenna, as calculated from these patterns is 6.3 db. over an isotropic radiator, or 4.2 db. over a very short dipole. The theoretical gain calculated from the theoretical patterns is 6.5 db. over an isotropic radiator. The gain at other frequencies is illustrated in Fig. 3, together with the variation of side lobes with frequency. An improved gain at 210 Mc. per sec. could be secured easily with little loss at 235 Mc. per sec. by increasing the dipole spacing and using a branched feeder as mentioned in "The Selected Design" above. The width of the vertical radiation pattern at half voltage points decreases steadily from 36 degrees at 210 Mc. per sec., to 31 degrees at 235 Mc. per sec.

For this application, in common with many others, the directive characteristics and the gain are not as important as the impedance variations of the antenna. The degree of antenna mismatch may be expressed as a voltage standing wave ratio in the transmission line. From this the range of impedances presented to the transmitter may be found readily, and excess line losses, reflection losses, etc., calculated.

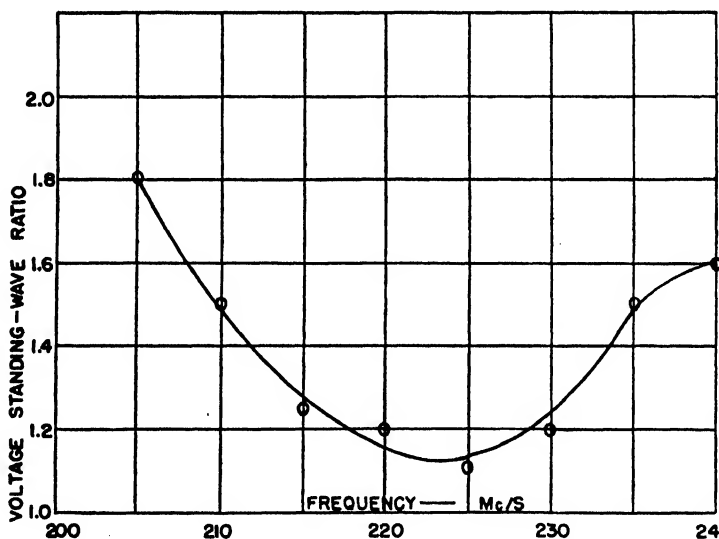


FIG. 4. The antenna match plotted against frequency.

Fig. 4 shows the variation of antenna match with frequency. Thus for a voltage standing wave ratio less than 1.2, we have about a 5% frequency band, and for a voltage standing wave ratio less than 1.5 we have a 10% band. It was not considered worth while to attempt to improve these results, although it was known that the dipoles were somewhat too short for resonance, and good broadband technique demands correction of each error as closely as possible to its source. However, the results obtained with this experimental arrangement point out the ease with which this type of antenna can be matched over a broad band of frequencies.

Further Possibilities

It is felt that this design of an omnidirectional, vertically polarized, antenna array could be adapted for use on wave lengths up to 10 m. and down to 10 cm. One or more pairs of half-wave dipoles could be connected up in this fashion. Perhaps the most useful form of this antenna would be one consisting of a single pair of half-wave dipoles, for frequency modulated broadcasting, television, or mobile services, which are generally at wave lengths of a few meters. A gain of nearly 3 db. over a half-wave dipole could be expected in a fairly simple structure.

The method of feeding the radiators in arrays of this type can be modified easily to suit individual requirements. For example, a concentric line may be continued on up the mounting pipe internally or even externally, and either lumped or distributed constant balancers used at the dipole feed points. Other methods of impeding the current induced on the mounting pipe are also available and may be applied in certain cases. One obvious method is to cut off the pipe near the position of the top choke. Again a suitable ground plane may be available, and it can be placed a quarter-wave below the mouth of the lower choke, which may then be omitted. It is felt, however, that the antenna described here is the most flexible arrangement to apply to problems where vertical polarization is required in the VHF band.

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SOME OBSERVATIONS ON FACTORS AFFECTING THE STRUCTURE OF CALCIUM SOAP LUBRICATING GREASE¹

BY L. W. SPROULE² AND W. C. PATTENDEN²

Abstract

Examination with the electron microscope indicates that the soap particles contained in calcium soap lubricating greases have an unusual structure. They are about 1 μ long, and consist of fibers coiled in spiral forms, or of two twisted together in a ropelike manner. The effect of two factors on the form of the dispersed soap particles was investigated. The addition of water to stabilize a dispersion of calcium soap in mineral oil was found to orientate the soap particles from minute, nondescript form to fibers having a wavy, loosely coiled appearance. The shearing action associated with the mixing of the grease during its preparation caused the fibers to assume a spiral or twisted form.

Introduction

Calcium base lubricating greases may be defined as three-component systems consisting of a dispersion of calcium soaps of the higher fatty acids in mineral oil stabilized by a small quantity of water. In view of the colloidal nature of such systems, considerable work has been carried out to determine the size and shape of the dispersed soap particles.

Attempts by Farrington and Davis (3) to photograph the soap particles using an ordinary microscope were unsuccessful. Galloway and Puddington (5, 6) tried to determine the nature of the soap particles by indirect methods, such as viscosity characteristics of soap-oil dispersions, observing the appearance of stream double refraction, etc., but were unable to clearly establish the nature of the particles. Recently Burton (1) has successfully used the electron microscope to indicate the form of the calcium soap particles. His pictures showed that the particles were approximately 1 μ long, and appeared to consist of tightly coiled fibers. Some time later Farrington and Birdsall (4) published electron microscope pictures of calcium soap lubricating greases which confirmed Burton's work. Ellis (2) has further clarified the structure of the calcium soap particles by comparing electron microscope pictures with X-ray photographs of brass-impregnated plasticene models. He concluded that the soap fibers have the form of a two-stranded rope.

While previous investigations have shown the size and structure of the soap particles contained in calcium soap greases, no information is available

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Contribution from the Technical and Research Department, Imperial Oil Ltd., Sarnia, Ont.

² Research Chemist.

to indicate the factors responsible for their unusual appearance. This paper describes experiments carried out to determine the effect of shearing forces present during the manufacture of calcium soap greases, and the effect of the presence of the water required to stabilize calcium soap - mineral oil systems on the shape of the soap particles of calcium soap lubricating greases.

Experimental Work

The effect of the presence of water and of the shearing forces present during manufacture on a calcium soap dispersion in mineral oil may be readily determined by electron microscope examination of samples removed at different stages of the preparation of a typical calcium soap grease.

In preparing the grease, calcium hydroxide is reacted with animal fat in the presence of a small amount of mineral oil at 149°C . (300°F .) and 50 lb. pressure. The "soap concentrate" formed is transferred to an open mixer, provided with a jacket through which steam or cold water is circulated. Agitation of the kettle contents is carried out by double-action paddles, and is continuous throughout the preparation. Mineral oil is added to the soap concentrate until a temperature of about 113°C . (235°F .) is reached. At this point the water necessary to stabilize the soap dispersion is added, generally in two portions. Sufficient mineral oil is now added to obtain a grease of the required consistency.

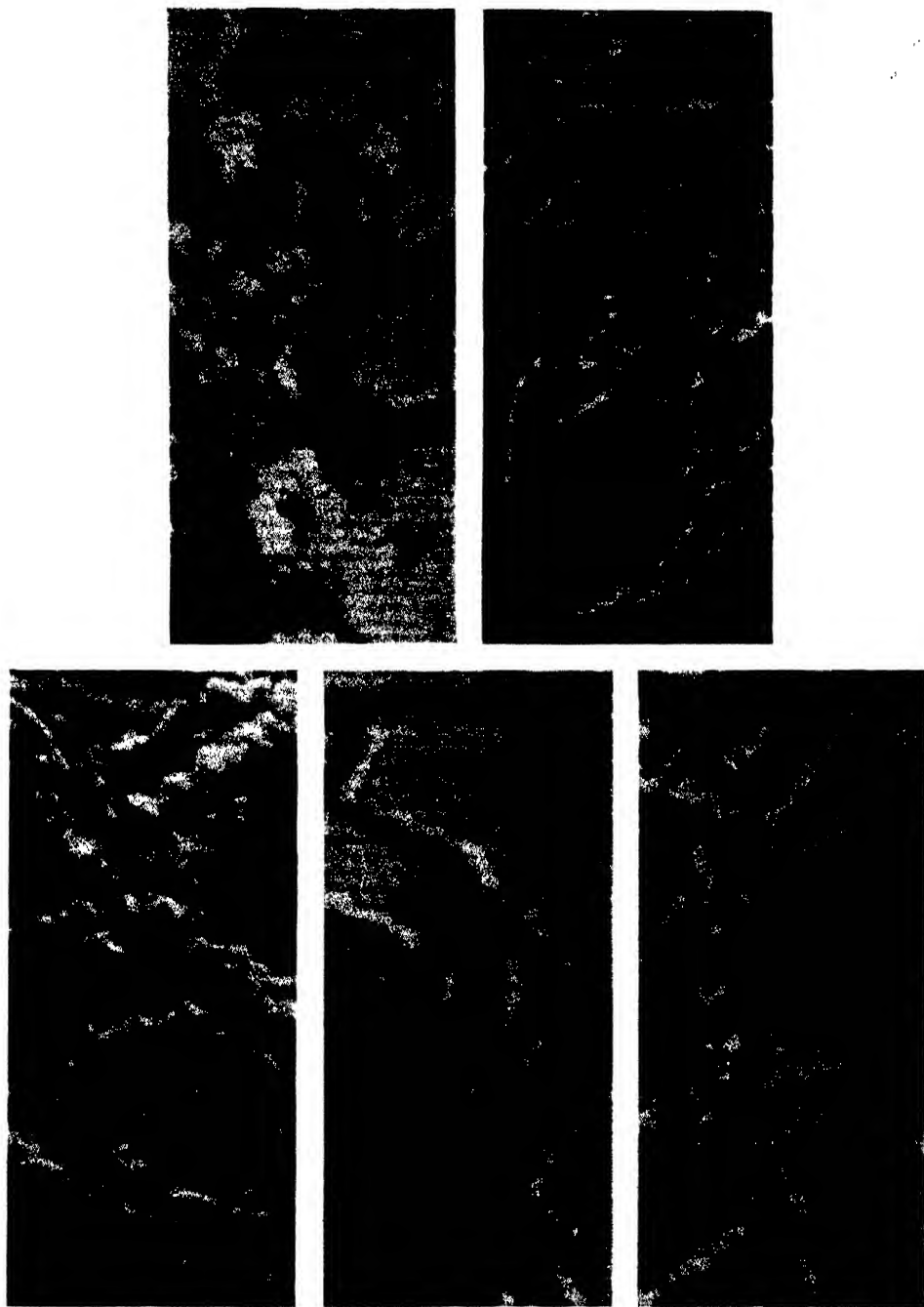
For the purpose of this investigation, five samples of grease were removed at different intervals during its preparation. Details of the samples are given in Table I. The samples were examined at room temperature with the electron microscope.

The samples studied in the preceding experiment were subjected to shearing forces during their preparation. To separate the effect of the two variables, water and shearing forces, a grease was made under conditions where shearing forces were entirely absent.

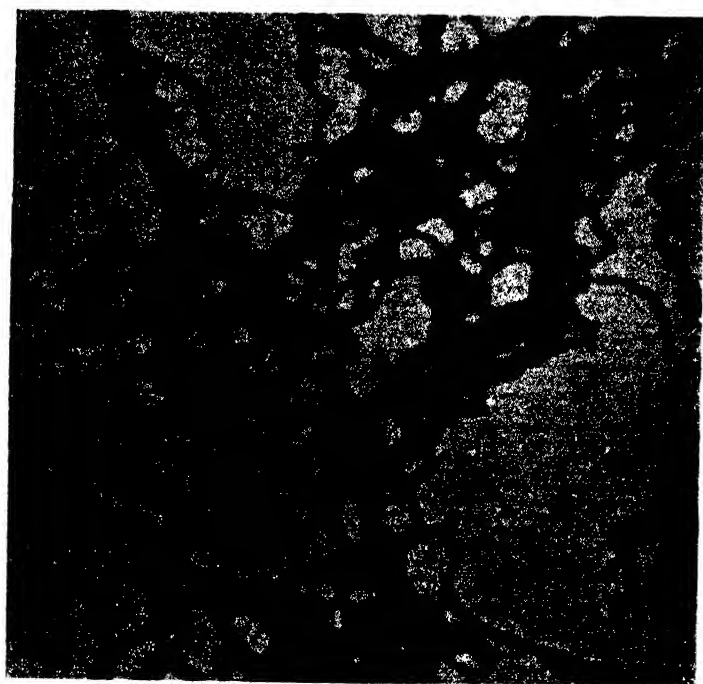
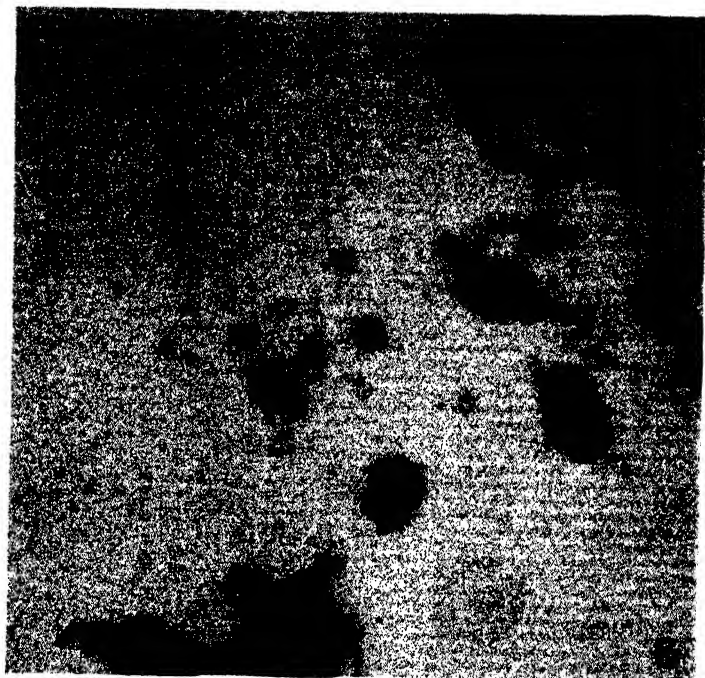
For this purpose a portion of the grease from the previous experiment was dehydrated by heating at 149°C . (300°F .) for 15 min. under a pressure of 1 mm. of mercury. Approximately 2 gm. of the dehydrated grease was transferred to one arm of a Y-tube. A few drops of water were placed in the second arm and the third arm sealed off. The section containing the dehydrated grease was heated in an oil bath, while that containing the water was maintained at -12°C . (10°F .) by means of a dry-ice bath. At 149°C . (300°F .) it was noted that the soap had settled from the mineral oil, and at 177°C . (350°F .) it was completely dissolved, except for a slight haziness. The grease was made by pouring the melted water into the soap-oil solution at 177°C . (350°F .). On cooling, a grease of good consistency was formed. The grease was examined with the electron microscope at room temperature.

The electron microscope photographs were made by the Department of Physics, University of Toronto. The smear mount technique, as described by Ellis (2) was used, except in those cases where further resolution of the

PLATE I



FIGS. 1-5. *Electron micrographs of samples of a calcium soap grease taken at various stages during manufacture. $\times 24,600$. FIG. 1, smear mount. FIGS. 2-5, shadow cast.*



FIGS. 6 and 7. *Electron micrographs of a calcium soap grease prepared without mixing.*
 $\times 28,600$. *Both are smear mounts.*

TABLE I

SAMPLES REMOVED FOR ELECTRON MICROSCOPE STUDY DURING MANUFACTURE
OF A CALCIUM SOAP LUBRICATING GREASE

Time from dropping of soap stock into open mixer, min.	Sample No.	History of sample	Appearance of sample when removed from mixer	Composition of grease					
				Parts of weight			% by weight		
				Calcium soap*	Water (added)	Mineral oil**	Calcium soap*	Water (by analysis)	Mineral oil**
0	—	Soap stock dropped into kettle	Thick, tacky, semi-fluid	13	0	2.9	81.8	0	18.2
60	—	29 parts oil added							
70	1	Sample removed at 113° C. (235° F.)	"	13	0	31.9	29	0	71
75	—	1.0 part water added							
85	2	Sample removed at 110° C. (230° F.)	"	13	1	31.9	28.3	2.0	69.7
95-130	—	12.6 parts oil added followed by 1 part water							
140	3	Sample removed at 104° C. (220° F.)	Greaselike	13	2	44.5	21.8	3.4	74.8
145	—	9.6 parts oil added							
185	4	Sample removed at 99° C. (210° F.)	"	13	2	54.1	18.8	2.8	78.4
190-360	—	30.9 parts oil added							
370	5	Sample of finished grease removed at 88° C. (190° F.)	"	13	2	85	13	1.6	85.4

* Inspections of animal fat used in preparation of soap—Saponification value: 196; Iodine No.: 52.8.

** Viscosity of mineral oil at 37.8° C. (100° F.): 65 cks.; Viscosity index : 75.

particles was desired. In these specimens, the shadow cast technique of Wyckoff and Williams (7, 8) using chromium was applied.

The effect of rate of cooling on the structure of the particles in calcium soap greases was not studied in detail. However, experience in plant manufacture has shown that those properties depending upon the nature of the soap particles, such as texture and consistency, are not altered by small changes in rate of cooling. In view of these observations, it is considered that differences in the rates of cooling of greases prepared in the two experiments described will have little effect. However, confirmation of this point awaits the completion of further laboratory investigation.

Results

The electron micrographs of the samples taken at various stages during the manufacture of a calcium soap grease are shown in Plate I. The picture of the anhydrous soap-oil dispersion (Fig. 1) indicated the soap to be present in the form of a large number of very fine particles or agglomerates of fine particles which have no regular size or shape. Fig. 2, taken after the first addition of water, showed the soap particles to be in the form of fibers. After the second addition of water (Fig. 3), the fibers appeared as loose coils. The addition of further quantities of oil caused the fibers to become more tightly coiled as the preparation of the grease proceeded (Figs. 4 and 5). The change in structure of the soap particles at this stage is not attributed to the addition of oil, but to the effect of the prolonged shearing action required to render the system homogeneous.

Plate II shows electron micrographs of the grease prepared without the use of a shearing action. Fig. 6 illustrates the shape of the soap particles contained in a dehydrated calcium soap grease. The soap was found to be present as very small particles, which confirmed the results of the first experiment. After the addition of water, the soap particles were orientated in the form of fibers, having a wavy or loosely coiled appearance. At present no explanation can be advanced for the wavy appearance of the soap particles, which appears to be characteristic of calcium soap-water-mineral oil systems. Attempts to correlate the appearance of the fibers with models corresponding to various molecular structures were unsuccessful.

From the data obtained in these experiments, it has been possible to account in part for the unusual structure of the soap particles in calcium soap greases. When calcium soap is stirred in mineral oil at elevated temperatures, it becomes dispersed in the form of minute, nondescript particles. The addition of water to this system orientates the particles in the form of fibers having a wavy or loosely coiled form. The shearing action associated with mixing causes the fibers to become tightly coiled.

Acknowledgment

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PRODUCTION AND PROPERTIES OF 2,3-BUTANEDIOL

XXVIII. PILOT PLANT RECOVERY OF *levo*-2,3-BUTANEDIOL FROM WHOLE WHEAT MASHES FERMENTED BY *AEROBACILLUS POLYMYXA*¹

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Abstract

Whole wheat mash fermented by *Aerobacillus polymyxa* was stripped of ethanol, screened, and concentrated. The resulting syrup was passed through a steam stripping column, and the *levo*-2,3-butanediol in the condensate was recovered by rectification. The composition of intermediate materials and products, performance of pilot plant equipment, and data and recommendations for the design of a large scale plant are given. Corrosive conditions are indicated and possible materials of construction suggested. A quantitative flow sheet and cost estimates for a commercial plant with a capacity of 1000 bu. of wheat a day are included. The daily output of such a plant is estimated to be 8460 lb. of diol (95.5% recovery), 675 gal. of 95% ethanol, 3900 lb. of dried bran, and 25,300 lb. of dried solubles. The initial cost of such a plant is estimated at \$500,000. From estimates of raw materials and energy requirements the total cost of production of diol is calculated to be 17.3 cents per lb. when wheat costing \$1.10 per bu. is fermented.

Introduction

The recoverable products of a grain mash fermented by *Aerobacillus polymyxa* are ethanol, *levo*-2,3-butanediol, and residual solids. *Aerobacter aerogenes* produces a smaller amount of ethanol and a correspondingly greater amount of diol which is predominantly the *meso*-isomer (22). The physical properties of the two diol isomers other than the freezing points of aqueous solutions are very similar; consequently, any method of recovery applicable to one could be applied to the other with only minor changes in the process.

Since ethanol is the lowest boiling constituent it is easily recovered by distillation. Diol, however, has a boiling point above that of water (179° C. or 354° F. at 760 mm.) and cannot be recovered by a simple distillation of the fermented mash. The initial steps of all suggested recovery methods are similar, and consist of removal of ethanol, filtration or screening, and concentration of diol and solids by evaporation. Ethanol can be recovered either by a separate operation or during evaporation. The former method was used in the pilot plant and the latter method is recommended by Callaham (5) for the recovery of ethanol from mashes fermented by *A. aerogenes* and has also been used to recover industrial ethanol from molasses fermented by yeast (17).

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The methods that have been suggested for the recovery of diol from evaporator syrup are spray drying (12), drum drying (12), chemical conversion (18), dialysis (7), solvent extraction (12, 13, 16), ethanol precipitation (21), kerosene distillation (12), and steam stripping (4, 5). The methods that have been tested in these laboratories will be briefly described.

Drum Drying.—This method was tested by J. D. Leslie and D. Rose in the experimental laboratory of the J. P. Devine Manufacturing Co. at Mount Vernon, Illinois, in 1943. It was found that with a vacuum of 28 in. of mercury and a steam pressure of 60 p.s.i. gauge, the lowest diol concentration that could be obtained in the dried solids was 7.6%. At higher steam pressures or lower drum speeds the solids began to decompose. Because of these results no further work was done on this method.

Dialysis.—Laboratory tests showed that large equipment would be required for large scale production. No work on a pilot plant scale was performed.

Ethanol Precipitation.—In this pilot plant, and elsewhere (21), syrup was first thoroughly mixed with ethanol, either with or without previous chemical treatment, the solids were allowed to settle, and the supernatant liquid was drawn off. Ethanol and diol were then recovered from the decantate by distillation. The remaining solids may be treated with ethanol a second time and then dried.

Steam Stripping.—In this method syrup and steam were passed counter-currently through a packed column, operated under pressure to favor vaporization of diol. A description of this method as applied to the recovery of the *meso*-isomer is given by Blom *et al.* (4), and a more complete flow sheet is given by Callaham (5). The present paper gives the results obtained in the pilot plant for recovery of *levo*-butanediol by steam stripping. In commercial production the diol would be condensed from the vapors leaving the top of the stripping column, by continuous countercurrent water scrubbing in a packed or plate column.

After the diol has been separated from the solids it must be freed of water and impurities. In commercial production the by-product ethanol would be concentrated and purified and the suspended and soluble solids would be dried. If the solids were to be dried separately, a rotary drier could be used for the suspended solids and a drum drier for the stripping column residue. As an alternative, the solids could be mixed and the mixture dried in a rotary drier.

The recovery units were designed for a capacity of about 900 gal. of mash per week, and the operations investigated included ethanol stripping, decantation, filtration, screening, evaporation, ethanol precipitation, steam stripping, purification, and drying. In addition to the results obtained in the pilot plant, a suggested quantitative flow sheet for the commercial production of butanediol together with estimates of fixed, material, and processing costs are included in this paper.

Pilot Plant Equipment, Operations, and Experimental Results

Fig. 1 is a diagrammatic flow sheet of the pilot plant showing the important vessels and flow paths. The vacuum distillation unit for purifying diol is not shown. The usual recovery procedure was to process the mash of two fermentations, about 900 gal., and to carry it through to the final recovery stages before starting another batch. Thus, although some of the units were designed for continuous operation, they were operated continuously only long enough to process one batch. Other operations, such as decantation and ethanol precipitation, were true batch operations.

Mash Composition

A description of the mashing and fermentation methods and results will be submitted in a subsequent paper (2). An initial mash concentration of approximately 15%, or 34 gal. per bu., was used for nearly all fermentations. A constant concentration was not obtained because of varying amounts of added water and sparged steam. Product concentrations in the fermented mash varied both for this reason and because of the fermentation conditions. To correct for variations in mash concentration, all yields and concentrations were calculated either to the basis of initial weight of wheat or to that of a 15% mash concentration. Assuming the initial wheat to be 50% starch, a fermentation efficiency of 90%, and a diol-to-ethanol ratio of 1.50, the fermented mash would be 2.32% by weight diol and 1.54% ethanol (2). A 60 lb. bushel of wheat would yield 8.91 lb. of diol and 5.91 lb. of ethanol. The fermented mash has a total solids concentration of 6.47%. Calcium carbonate added to the mash accounted for about 10% of the total solids, and the remainder was unfermented material from the wheat and malt. About one-half of the solids was soluble and an amber colored liquid was obtained on filtration. The specific gravity of the fermented mash was 1.020 and that of the filtrate was 1.010. Fermented mash also contained small amounts of diacetyl, acetoin, organic acids, and unfermented carbohydrate. The method used to analyze fermented mash and other pilot plant products has been described (11).

Ethanol Recovery

The first step of the recovery process was to strip ethanol from the fermented mash in a copper, bubble cap, beer column. The column was 2 ft. in diam. with 22 plates on 17-in. spacings. Each plate had 14 bubble caps which, except for those of the top two plates, were not slotted. Instead of slots, the edges of the caps were $1\frac{1}{4}$ in. from the plates. This construction was used because bran particles would have plugged the slots. Ethanol was removed at a concentration of 150 proof, and was passed through a cooler, rotameter, and tail box to a 750 gal. steel storage tank. Heat was supplied at the base of the column by either a steam coil or steam sparge. (During operation only the coil was used, but sparged steam was necessary in starting up.) The feed rate to the column was controlled with an orifice meter and controller. The steam supply was automatically controlled by the pressure drop across the

column and the slops discharge was controlled by a liquid level controller in a tank opposite the base of the column. The distillate composition was regulated manually according to the temperature at the top of the column and the hydrometer reading of the material in the tail box. The ethanol content of the slops was estimated by condensing a portion of the vapors below the bottom plate and determining the ethanol concentration with a hydrometer, as is the practice in the production of industrial ethanol and distilled liquors.

The feed rate to the beer column was 200 to 250 gal. per hr. or 65 to 80 gal. per hr. per sq. ft. of cross section. The unit gave satisfactory performance when fed at either the eleventh or fifteenth plate from the bottom. During the operating period, when conditions were steady, the unit was operated at a reflux ratio (reflux rate divided by take-off rate) of 10 and a product concentration of 150 proof. The high wine contained 0.1% diol, which is a diol loss of 0.08%; and the slops contained 0.01% ethanol, which is an ethanol loss of 0.67%. The plate efficiency of the column was 25%. A low value was expected for this column because of the construction of the bubble caps of the bottom 20 plates.

No difficulty was experienced in transferring sufficient heat to the boiling slops, and heat transfer coefficients of the order of 400 to 500 B.t.u. per hr. per sq. ft. per °F. at a temperature difference of 45° F. were obtained. The nominal retention time in the beer column was 12 to 15 min.

The composition and purification of the high wine obtained from the ethanol stripping operation has been discussed by Tollefson, Wheat, and Leslie (19).

SUSPENDED SOLIDS REMOVAL

Decantation and Filtration

After about 16 hr. settling in the holding tank, approximately 60% of the slops could be decanted as a clear liquid. The thickened slops were filtered with an Oliver vacuum filter of the rotary, precoat type, with a drum 3 ft. in diam. and 2 ft. long. After numerous operational difficulties caused by foam had been eliminated, filtration rates of 3 gal. per hr. per sq. ft. were obtained. Filtration was abandoned because of large diol losses (3 to 6%) and the high precoat content of the filter cake. Instead, a simple screening operation was used.

Screening and Pressing

In these operations whole slops were screened and the resulting solids were pressed to remove a large portion of the liquid phase. The vibrating screen was a Model 35 Dillon, 1.5 ft. wide and 4 ft. long. It was operated at approximately 30 vibrations per second by means of an eccentrically weighted fly wheel. A section of the screen, 2 in. wide, was used for washing experiments. Wash water was distributed from three 1 in. pipe caps placed longitudinally along the screen. Each cap was drilled with five 1/32 in. holes and the amount of wash water was measured with a rotameter. The washings were mixed with the screen filtrate. Wet bran fell through a chute to the press

on the floor below. This press consisted of a pair of washing machine wringers driving an endless belt of 60 mesh screen which carried the bran between the wringers.

Tests were made on the vibrating screen with both 40 mesh and 100 mesh screen. The difference in performance between the two was insignificant, showing that solids not removable by filtration are present in slops in two definite particle sizes: those retained by 40 mesh and those that pass 100 mesh. For calculating material balances and studying screening data, solids that pass 100 mesh were arbitrarily defined as soluble. The ratio of insoluble solids to total solids in slops was determined from the mean value of 18 tests of the ratio of total solids in slops to total solids in screen filtrate. From these results it was found that 13% of the solids in slops was insoluble. The screen could be operated at 5000 gal. per hr. per ft. of width without overloading but in pilot plant tests, other than washing experiments, lower rates were used.

It can be shown by theoretical calculation that the percentage diol and soluble solids retained by the screen are functions of only the total solids in slops, screen filtrate, and screenings; or of the insoluble solids in slops and screenings. At a constant ratio of insoluble to total solids in slops and a constant total solids content of screenings, the percentage diol and soluble solids retained by the screen increases with increasing solids content of slops, regardless of the initial diol concentration. Since the total solids content of slops varied throughout each run as well as from one run to another, a variable screen performance was obtained. Because the screen was seldom operated at full capacity, variations in the composition and rate of feed could not be expected to affect the solids concentration of the screenings. Therefore, the value obtained in the pilot plant should be applicable to large scale operations in which the screen is not overloaded. In 13 tests, this value varied from 12.8 to 15.6% with a mean of 13.5%. The average amounts of diol and total solids retained on the screen were 5.5% and 15.3%, respectively. These values varied from 3 to 7% for the diol retained and from 9.5 to 21% for the solids.

Most of the liquid in the screenings was very loosely bound and could be removed by a mechanical pressing operation similar to that used in distilleries. The results obtained with the washing machine wringers corresponded to those obtained with commercial types of presses. After pressing, the screenings had a solids concentration of about 31%. This means that 75% of the liquid phase, and therefore 75% of the diol, was recovered by pressing.

In commercial production it would be desirable to decrease the diol content of the bran in order to increase recovery and also to improve the quality of the bran as a livestock feed. The simplest method of accomplishing this is to wash the bran as it moves across the screen. To evaluate the experimental results, they were compared with the theoretical results of one equilibrium contact. In the calculations it was assumed that washing would not change the total weight of screenings, i.e., that the insoluble solids concentration of

the screenings would not change. Amounts of water varied from 9 to 19% of the slops and recoveries varied from 50 to 100% of one equilibrium contact. A more efficient system of water distribution would improve washing performance and for large-scale production a screen at least 6 ft. long, with wash water well distributed over the middle third, is recommended.

EVAPORATION AND RECTIFICATION

Filtrate from either the filter or vibrating screen was pumped to the kettle, which consisted of a mild steel cylindrical shell with a steam coil of 80 ft. of 1½ in. copper tubing. It was charged with approximately 100 gal. of filtrate and, as evaporation proceeded, feed was added by manual regulation. From one to two liters of Turkey Red Oil was added to the initial charge.

The vapors from the kettle entered the rectifying column either at the base or near the middle. The reboiler of the column was a calandria type heating element consisting of 31 one-inch tubes 15 in. long. The condensate was pumped to the instrument panel where both reflux and take-off were manually controlled and measured with rotameters. The steam supplied to the kettle was automatically controlled by the pressure drop across the column. The column could be operated at automatically controlled pressures below atmospheric but nearly all evaporations were carried out at atmospheric pressure. Because of the very slight increase in boiling point with increasing diol concentration, temperature cannot be used to regulate reflux and take-off. Instead, the reflux ratio must be set and the column performance determined by material balances.

When the syrup was to be treated with ethanol, the vapors from the kettle were fed to the middle of the column and a portion of the diol removed at the base. Since the amount of diol vaporized was very small, particularly at the beginning of a run, diol was not withdrawn continuously but only whenever the temperature at the bottom of the column indicated a diol concentration of 60 to 80%. If the syrup was to be steam stripped, the vapor from the kettle was fed to the bottom of the column, the calandria was not used, and only water was removed. In either method, after all of the filtrate had been added to the kettle, evaporation was continued until approximately the desired solids concentration had been reached. The syrup was then blown with compressed air to the syrup storage tank.

Evaporation

The evaporation of decantate plus filtrate, slops, and screen filtrate was studied in the pilot plant. The distillate from all three materials was essentially water but also contained diol and some of the more volatile compounds formed during the fermentation and subsequent treatments. The diol content depended upon the operation of the rectifying column and will be discussed below. The most important of the impurities was an appreciable amount of acid. Most distillates were at a pH of from 3 to 5 and contained up to 0.4% acid expressed as weight per cent acetic acid. This material was found to be very corrosive to iron pipe, especially at points of contact with copper or brass.

Decantate and filtrate were occasionally concentrated to 50 or 60% solids but the syrup so formed was very viscous and difficult to handle. A solids concentration of 40% would be more satisfactory both for the evaporation and for the following operation. A large number of measurements of the over-all coefficient of heat transfer to boiling beer were made. These are not directly applicable to larger evaporators constructed of tubes rather than a coil but some useful information was obtained. The heat transfer coefficient to boiling water, determined immediately after the coil had been cleaned with a boiling 2% sodium hydroxide solution, was 750 B.t.u. per hr. per sq. ft. per °F. at a temperature difference of 15° F. and 920 at a difference of 20° F. The heat transfer coefficient decreased during evaporation and consequently the temperature difference increased to maintain a constant rate of boiling. This decrease in the coefficient was caused by increasing solids concentration and fouling of the coil. No attempt was made to differentiate between the effect of solids concentration and that of fouling in the evaporation of filtrate or slops, but an estimate of the effect of fouling in the evaporation of screen filtrate was made and is discussed below. The heat transfer coefficient to boiling filtrate at the start of an evaporation varied from 100 to 500 and at the end from 60 to 200 B.t.u. per hr. per sq. ft. per °F. The initial value depended on the cleanness of the coil and to some extent on the composition of the filtrate. After each run the kettle was washed with hot water and occasionally with sodium hydroxide. It was also washed at frequent intervals with ethanol when high wine was rectified.

It was more difficult to evaporate slops than filtrate. Only three tests were made, one at atmospheric pressure, another at 15 in. of mercury vacuum, and a third at 25 in. vacuum. At atmospheric pressure, the initial heat transfer coefficient was 500 B.t.u. per hr. per sq. ft. per °F. but it decreased rapidly after the solids concentration had reached 16% and at 20% the coefficient was 16. At 15 in. vacuum the coefficient was about 200 until a solids concentration of 22% was reached and then it decreased to 13 at 26%. At 25 in. vacuum the coefficient was 70-90 to a solids concentration of 40% and then decreased to 36. The evaporation of slops is not practical because of the low heat transfer coefficients and also because of the difficulties that would be encountered in handling syrup containing large particles of bran.

Screen filtrate was evaporated more easily than slops but with greater difficulty than filtrate. The resulting syrup, however, contained no large particles and was not appreciably more difficult to handle than the syrup from decantate and filtrate. Solids concentrations of from 35 to 40% have been obtained but 30% would be recommended for commercial production for ease of handling and to reduce decomposition and fouling in the evaporator. The initial value of the over-all coefficient of heat transfer varied from 300 to 500 and the final value from 20 to 200 B.t.u. per hr. per sq. ft. per °F. It was observed that the heat transfer to material containing large amounts of unfermented starch was appreciably lower than that to material from complete fermentations. Hot water washes between runs did not clean

the coil thoroughly after the evaporation of screen filtrate and it was necessary to use sodium hydroxide after each run. Even then, a thin, hard film, removable by scraping, formed on the coil over a period of approximately six months.

To determine the extent of fouling and diol decomposition, screen filtrate concentrated to 20% solids was refluxed until the heat transfer coefficient was below 100. A plot of the coefficient against time (Fig. 2) shows that fouling occurred rapidly. The extent of solids deposition and fouling would be

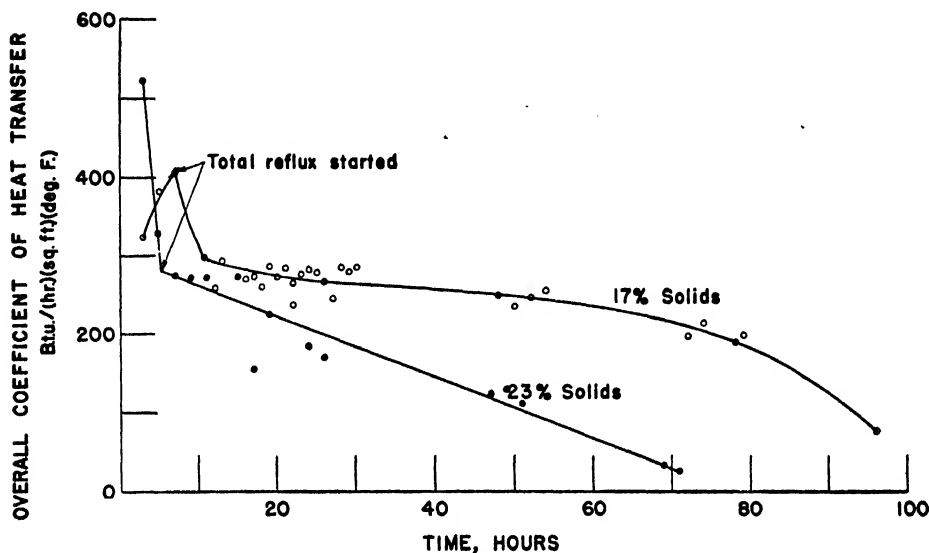


FIG. 2. Decrease in the over-all coefficient of heat transfer on refluxing partially concentrated screen filtrate.

reduced in forced circulation, long tube evaporators, but frequent washing of the tubes with sodium hydroxide, and mechanical cleaning at longer intervals, would probably be necessary. To determine whether or not diol decomposition was appreciable, material balances were made over the whole operation. For reflux times of 25, 52, and 96 hr. the diol losses were 3.2, 9.7, and 4.5%, respectively. These experiments show that some diol decomposition occurs but it would not be appreciable in commercial production where the retention time of an evaporator would be relatively short compared with that used in these tests.

In this work the diol concentration of the distillate ranged from 0.4 to 0.14% and losses were about 5%. Reflux ratios (reflux rate divided by take-off rate) of about 0.5 were used in most evaporations. The plate efficiency of the rectifying column was tested with both diol-water and ethanol-water systems and was found to be approximately 25%. In view of the low efficiency of the rectifying column, the most reliable method for designing columns for commercial production would be to use accurate vapor-liquid equilibria data and the usual methods of estimating allowable vapor velocities and plate efficiencies.

Rectification

In this operation diol losses in the distillate were appreciably greater than for evaporation because there were fewer plates above the feed. At a reflux ratio of 1.0 losses were approximately 15%. At temperature differences of about 70° F., over-all coefficients of heat transfer of about 250 B.t.u. per hr. per sq. ft. per °F. were obtained in the reboiler. About one-half of the diol was removed from the reboiler at a concentration of 40 to 70%. This material was dark green or brown in color and in addition to diol and water it contained organic acids both free and combined, ammonia and other nitrogen compounds, and solids. The presence of solids was due to entrainment from the kettle to the rectifying column. Analysis of a typical crude diol showed 4.5 lb. of ammonia; 4.25 lb. of free acid and 0.6 lb. of ester, calculated as acetic acid; and 1.5 lb. of solids per 100 lb. of diol.

DIOL RECOVERY

Ethanol Precipitation

Syrup was mixed with 95% ethanol in the syrup storage tank and the mixture was allowed to settle. In a few tests the addition of ethanol was preceded by the addition of lime. After settling, the decantate was pumped off and recycled with fermented mash, or diol and ethanol were recovered by distillation. The solids were removed from the tank and filtered through three or four layers of cheese cloth. The solids were discarded and the filtrate was added to the decantate.

Although ethanol extracted a large portion of the diol it also extracted an almost equally large portion of the solids. In most tests the precipitated solids settled rapidly to an easily handled granular precipitate, with a sharp layer between solids and decantate. The mean of six tests showed that 83.3% of the diol and 76.7% of the solids were extracted. In one test, in which the syrup was first treated with lime, 94.5% of the diol and 33.7% of the solids were extracted. A lime treatment, therefore, would be used industrially and the first precipitate would probably be retreated with ethanol. Ethanol would be recovered from the decantate by distillation and the resulting crude diol could be treated in several ways. Walmesley and Davis (21) propose a vacuum distillation and report an over-all recovery of diol from fermented molasses of 90%. It is doubtful whether a vacuum distillation could be successfully applied at this stage of the process for the recovery of diol from whole wheat mashes. The diol-to-solids ratio would be about 0.85 while that reported by Walmesley and Davis is 2.5. The composition of the solids extracted by ethanol differed from that of the precipitated solids since in one test the decantate contained 81% of the nitrogen and 72.5% of the solids of the syrup. Therefore it is not advisable to recycle the diol-solids mixture with syrup because of the risk of increasing the ethanol soluble solids to such an extent that the method would no longer be practicable.

Steam Stripping

The steam stripping column consisted of a 20 ft. length of 6 in. pipe. Initially, 1 in. raschig rings were used as packing but they were replaced as soon as $1\frac{1}{4}$ in. spheres were available, although there was no evidence that rings were not satisfactory. After about a year of operation with spheres and with syrup from screen filtrate, the packing was found to be partially plugged and the raschig rings were replaced. A steam flow controller was installed at the inlet to the column and the pressure at the top of the column was controlled at 40 p.s.i. gauge. Considerable difficulty was experienced in securing a constant feed rate because of the high viscosity of syrup and the low flow rates required. In July, 1947, a proportioning pump was installed and syrup was pumped from an open tank in which volume measurements were made. The syrup was screened through 60 mesh wire cloth to prevent large particles of rust from plugging the check valves of the pump.

Syrup was preheated by a 6 ft. steam jacket around the feed pipe. The residue at the base of the column was collected in a vessel under pressure, and at intervals this vessel was isolated from the column and the residue drained. A float type, liquid level controller installed in February, 1947, proved to be more satisfactory. The residue was usually discarded but a number of drum drying tests and analyses of the dried material were performed. The vapor from the top of the column was condensed and concentrated in the kettle before purification by vacuum distillation.

The results obtained with syrup from decantate and filtrate are shown in Table I. At the time, it had not been possible to maintain a constant feed

TABLE I

STRIPPING COLUMN RESULTS ON SYRUP FROM DECANTATE AND FILTRATE

(Operating pressure: 40 to 42 lb. per sq. in. Column packed with 1-in. raschig rings)

Feed rate, lb. per hr. per sq. ft.	44	111	204	503	505*
Steam rate, lb. per lb. feed	26.2	16.4	5.7	2.3	3.0
Recovery, %	80.5	97.1	92.5	98.1	99.2

* Column packed with $1\frac{1}{4}$ -in. spheres.

rate to the column over long periods. To secure the information presented, samples of condensate and residue were collected over one-hour periods during which the feed rate appeared to be constant. Material balances were calculated from the analyses of the four fluids entering and leaving the column and from the volume of condensate. The calculated residue rate was then compared with the measured rate, and in all the tests reported in Table I the agreement was within 8%. Neither height of a theoretical plate nor height of a transfer unit was calculated with these data and none of the stripping column residue was retained for drying tests.

The accumulation of material in the column partially plugged the packing, and the pressure drop increased until eventually the column flooded and syrup was carried over the top with the diol-water vapor. This accumulation of material was not caused by excessive liquid or vapor rates but by the nature of the syrup. The only method by which diol could be steam stripped from syrup was to operate the column until flooding occurred and then to wash out the accumulated solids. This procedure was followed to determine how long the column could be operated under various conditions before flooding. The extent of accumulation was followed by observing the pressure drop across the column throughout a run. The pressure drop increased slowly from about 0.5 in. of water per foot of packing to 1.5 in. and then increased rapidly to 5.5–7.0 in., when flooding occurred and solids were entrained by the vapor at the top of the column. When direct measurement of the feed was possible, samples were taken over several one-hour periods during each run for analyses and calculation of material balances. Total material and diol balances generally checked to within experimental error, but there was a consistent loss of about 15 to 30% of the solids fed to the column at a solids concentration of 18.5%, and a 25 to 50% loss at a solids concentration of 23.6%. The solids were removed at the end of a run by running water at 40° to 50° C. at a rate of 1750 gal. per hr. per sq. ft. through the column for half an hour. During shutdown periods the column was left full of water. From the fact that the initial pressure differential did not steadily increase it is concluded that this procedure is sufficient to clean the column and that cycles can be repeated indefinitely.

The flooding times at various syrup solids contents and operating conditions are given in Table II. Flooding times at rounded values of solids content and feed rate were obtained by interpolation and are given in Table III.

From the analyses of the samples taken over one-hour periods the values of $(H_t)_{og}$ were calculated and are given in Table II. Equation (1) for equimolar counter diffusion given by Colburn (6) was used to calculate the number of transfer units.

$$(N_t)_{og} = \int_{y_1}^{y_2} \frac{dy}{y^* - y} \quad (1)$$

$(N_t)_{og}$ = Number of transfer units based on change in gas concentration.

y = Mole fraction of diol in the vapor.

y^* = Equilibrium mole fraction of diol in the vapor.

The height of a transfer unit was then calculated from Equation (2)

$$(H_t)_{og} = \frac{H}{(N_t)_{og}} \quad (2)$$

H = Height of packing (17 ft. in the pilot plant column).

The vapor-liquid equilibria data of Tomkins *et al.* (20) at 45 and 75 p.s.i. abs. were interpolated to obtain the equilibria data at 55.7 p.s.i. abs., which was the average of the top and bottom pressures of the column. To estimate

TABLE II

FLOODING TIMES AND TRANSFER UNIT HEIGHTS AT VARIOUS OPERATING CONDITIONS OF THE STRIPPING COLUMN

Syrup solids, %	Syrup rate, lb. per hr. per sq. ft.	Steam rate, lb. per hr. per sq. ft.	Flooding time, hr.	$(H_L)_{OG}$, ft.
14.5	277	745	4.8	1.7
	293	680	4.3	—
17.0	169	610	12.3	4.0
	214	610	6.2	—
	223	680	9.0	2.0
18.5	161	610	14.8	3.7
	163	680	8.5	3.2
19.6	177	610	7.1	—
	168	610	5.2	—
	174	680	4.5	—
	164	745	2.6	—
	231	680	3.4	—
19.9	212	610	4.5	—
23.6	145	610	7.0	4.6
	148	680	4.3	4.6
	206	610	4.3	2.9

TABLE III

EFFECT OF SOLIDS CONTENT OF SYRUP ON THE FLOODING TIME OF THE STRIPPING COLUMN AT VARIOUS FEED AND STEAM RATES

Rates lb. per hr. per sq. ft.	Syrup 160	Steam 610	Syrup 210	Steam 610
Solids content of syrup, %	Flooding time, hr.			
17.0	12.3		6.2	
20.0	9.0		4.5	
23.6	6.2		4.3	

the diol concentration in the vapor in equilibrium with syrup it is necessary to know the effect of solids on the relative volatility of diol and water. Direct tests were performed in the Othmer still described by Tomkins *et al.* (20) to determine the effect of solids. The still was operated at atmospheric pressure, and, because of the foaming in the still, solids concentrations lower than those of actual syrups had to be used. The results obtained are given in Table IV. A closer approximation to the equilibrium diol concentration in the vapor is obtained by calculating the diol concentration in the liquid on a solids-free

TABLE IV

EFFECT OF SYRUP SOLIDS ON THE RELATIVE VOLATILITY OF DIOL AND WATER

Solids content, weight %	Liquid composition, wt. % of diol	Equilibrium vapor composition for pure solutions (20), wt. % diol	Observed vapor composition, wt. % diol	Variation, %
4.94	Total basis 2.08 Solids free basis 2.19	0.28 0.29	0.33	+15
11.50	Total basis 4.20 Solids free basis 4.76	0.58 0.66	0.68	+15 +3

basis rather than a total basis. Blom *et al.* (4), however, report that the solids should be considered as water, that is, that a total basis should be used.

The estimates of $(N_i)_{00}$ given in Table II are only approximate because the syrup was fed to the column at 185° F. rather than the boiling point of 287° F. and because of heat loss from the column. Cold feed increased the actual liquid rate in the column by 9.5% and heat loss increased liquid rate by about 40% at a feed rate of 160 lb. per hr. per sq. ft. The vapor rate at the top of the column was less than the steam rate by the amount of steam required to heat the feed and to supply the heat loss. Condensation at the top of the column to heat the feed would give a lower diol concentration in the exit vapor than that actually existing at the top of the packed section and would also make the actual diol concentration in the liquid lower than the diol concentration of the syrup. Thus, if actual concentrations at the top of the packing could have been used, values lower than those given in Table II would have been obtained for $(H_i)_{00}$.

The over-all coefficient of heat transfer from steam to syrup was determined in an experimental heat exchanger consisting of a $\frac{3}{8}$ and a 1 in. I.P.S. pipe in a 4 in. I.P.S. steam jacket. The rate of heat transfer was determined from the syrup rate and the increase in temperature of the syrup. The specific heat of the syrup was assumed to be 0.8 B.t.u. per lb. per °F. The results obtained are given in Table V.

TABLE V

HEAT TRANSFER FROM STEAM TO EVAPORATOR SYRUP

(Diol content of syrup, 10.26%; solids content of syrup, 25.1%)

Steam temperature, °F.	275	248	275	275
Mean temp. difference, °F.	153	144	150	150
Syrup rate, lb. per hr. per sq. ft.	70400	85600	76900	17000
Over-all heat transfer coefficient, B.t.u. per hr. per sq. ft. per °F.	167	127	181	22

CONCENTRATION OF STRIPPER CONDENSATE AND PURIFICATION OF CRUDE DIOL

The stripper condensate had a diol concentration of from 1.5 to 2.0% by weight, the remainder being mainly water and finely divided solids. It contained 7 to 10 lb. of acid, calculated as acetic acid, per 100 lb. of diol, and about the same amount of ammonia. The ester content was usually negligible because of the high water concentration. The condensate was evaporated in the beer kettle and rectifying column and water taken off overhead. This operation concentrated the diol and solids to form a crude diol. The evaporation was continued until the volume of crude diol was 25 gal. or less, as this volume was easily handled in subsequent operations. Because of the acidity of the condensate nearly all of the ammonia remained in the crude diol. A portion of the acid, however, was removed in the distillate. The crude diol obtained in the pilot plant contained both dissolved and suspended iron compounds resulting from corrosion of the kettle. The composition of several crude diols is given in Table VI.

TABLE VI
COMPOSITION OF CONCENTRATED STRIPPER CONDENSATE

Diol, wt. %	Lb. per 100 lb. of diol				Iron, molar
	Solids	Acid*	Ester*	NH ₃	
29.0	—	6.63	—	—	—
12.7	35.6	5.21	2.61	—	—
44.2	9.85	4.73	0.0	1.71	0.06
27.6	—	6.02	6.95	1.65	0.04

* Calculated as acetic acid.

Crude diol was vacuum distilled in a small copper unit that consisted of a 25 gal. steam jacketed still pot and a 10 ft. column 6 in. in diam. packed with $\frac{1}{2}$ in. raschig rings. Vapor from the still pot was admitted to the middle of the column. At the top of the column a coil provided reflux and at the bottom a steam jacket served as a reboiler. The unit was always operated batchwise and, to obtain better control, diol was removed from the top of the column rather than from the bottom. The steam to the reboiler was turned on full and two fractions, water and diol, were distilled, condensed, and collected in copper receivers.

Crude Diol from Rectifying Column

In purifying crude diol obtained from the base of the rectifying column, one distillation over sodium hydroxide, sufficient to neutralize the free and combined acid and to liberate the ammonia, reduced the total acid and ammonia to a negligible amount (0.02%). The evolved ammonia attacked the copper unit, and the water fraction was the deep blue color of the copper ammonium

complex. Calcium hydroxide was not satisfactory as a neutralizing agent because an excessive amount of sludge was formed and a large portion of the diol remained in the residue in the still pot. When sodium hydroxide was used, the contents of the still pot could be evaporated to almost complete dryness. The diol obtained by distilling the crude material over sodium hydroxide was a light brown color and two or three redistillations were required to produce a water white product. One distillation over sulphuric acid gave a clear product but dehydration products such as methyl ethyl ketone were formed (14). Even when colorless diol was prepared either by distillation over sulphuric acid or by repeated distillation over sodium hydroxide a color developed on standing.

Crude Diol from Stripper Condensate

The crude diol from stripper condensate was first distilled to separate the diol from the solids. Sodium hydroxide was not added to the crude because it caused excessive foaming during the distillation. The partially concentrated diol was then analyzed and sufficient sodium hydroxide was added to neutralize acids, saponify esters, liberate ammonia, and precipitate iron and copper. In the first distillation a sharp fractionation of acid occurred, giving a water fraction that was generally basic to phenolphthalein and a diol fraction with an acidity greater than that of the crude diol. Little or no decrease in total acid resulted. Both fractions contained some of the original ammonia but there was a loss of ammonia through the vacuum system during the distillation. Only traces of iron were found in the distillates, showing that iron was left with the residue of solids in the kettle. The water fraction, being slightly basic and ammoniacal, was always blue in color. The diol fraction, although usually containing considerable ammonia, was more acid than the other fraction and so had a lower copper content and a less intense blue color.

In the second distillation, carried out over sodium hydroxide, most of the acid, ester, and ammonia was removed. The water fraction was about 1% diol and the diol fraction was about 5% water. The water fraction was practically neutral and contained little or no ester. The diol was found to be uniformly low in acid and ester, about 0.01 *N* in acid and 0.02 *N* in ester. Ammonia was removed quite effectively and the amount left was almost entirely in the water fraction, leaving about 0.01 *N* ammonia in the diol as a maximum. This diol was either pale green to blue or colorless, and cations were present only in traces. Analytical data for one purification are presented in Table VII. The acid in the crude diol was 6.05% by weight of the diol present, expressed as acetic acid, and the acid content of the final product was 0.04%. Ester in the crude diol was 6.98% and was reduced to 0.09%. Ammonia was reduced from 1.65% to 0.01%.

Two samples of stripper condensate were purified by ion exchange resins in laboratory columns. Stripper condensate was used for the tests, as a dilute solution of diol must be used to maintain a low ester concentration. In commercial production where a scrubbing column would be used, the

TABLE VII

PURIFICATION OF CRUDE DIOL BY DISTILLATIONS OVER SODIUM HYDROXIDE

Material	Gal.	Diol, wt. %	Acid, N	Ester, N	NH ₃ , N	T.N.E.*	Color
Crude diol	11.0	27.6	0.277	0.320	0.268	0.953	
First distillation							
Water	4.7	0.04	Basic		0.023	0.023	Blue
Diol	6.0	52.9	0.456	0.00	0.434	0.890	Green blue
Second distillation**							
Water	4.25		Basic		0.087	0.087	Grey
Diol	1.80		0.011	0.011	0.010	0.032	Pale green

*T.N.E. = Total neutralization equivalent = Sum of acid, ester, ammonia, and ferrous iron normalities.

** Sufficient sodium hydroxide to neutralize the acid, ester, ammonia, and iron and a 10% excess was added.

product from the bottom of the scrubbing column would be passed through the exchanger beds. In the laboratory the condensate was passed through two cation exchangers in series and then through an anion exchanger column. The effluent was concentrated in a copper still to obtain a crude diol. This was further concentrated in glass apparatus and the diol was then distilled.

TABLE VIII

PURIFICATION OF STRIPPER CONDENSATE BY ION EXCHANGE RESINS

Condensate:		
Diol, wt. %	1.64	1.88
Acid, normality	0.0156	0.0286
Ester, normality	0.00025	0.000
Acid, lb. m. eq. per 100 lb.	1.56	2.86
Ester, lb. m. eq. per 100 lb.	0.025	0.0
Acid, lb. m. eq. per 100 lb. diol	95.2	152
Ester, lb. m. eq. per 100 lb. diol	1.52	0.0
Crude diol:		
Diol, wt. %	27.8	16.0
Acid, lb. m. eq. per 100 lb. diol	3.54	2.84
Ester, lb. m. eq. per 100 lb. diol	0.98	1.84
Acid, lb. HOAc per 100 lb. diol	0.21	0.17
Ester, lb. HOAc per 100 lb. diol	0.059	0.11
Cations exchanged,		
lb. m. eq. per 100 lb. diol	63.1	68.2
Anions exchanged,		
lb. m. eq. per 100 lb. diol	159	220

The data for these experiments are given in Table VIII. The sum of the cations and anions exchanged is greater than the sum of the initial acid and ester because of the presence of inorganic salts in the condensate. A small amount of ferrous iron was present but the excess cations removed were largely ammonium ions. The diol obtained from the condensate of one test was distilled at atmospheric pressure. The high temperature resulted in the decomposition of organic material which was not removed by the exchangers, and the diol was a pale yellow in color. The diol from the second test was distilled at reduced pressure and a water white product, which has remained colorless on standing, was obtained. Although the acid and ester content of the diol obtained in these experiments was higher than that of diol purified by distillation over sodium hydroxide, the ion exchangers appear to have removed the impurities that cause color and unpleasant odor. If desired, the acid and ester content could be further reduced by conducting the final distillation over sodium hydroxide. From the required exchange capacities given in Table VIII the cost of an ion exchange process for diol purification was estimated to be 1.6 cents per pound. However, the additional cost over direct neutralization during distillation is about 0.4 cents per pound.

A water white product can be obtained by treatment with ion exchange compounds and distillation at reduced pressure in corrosion resistant equipment. Distillation over sodium hydroxide in copper equipment gives a product that has a pale yellow green color and is very low in acid, ester, ammonia, and metallic compounds.

Heat transfer coefficients from steam to boiling diol-water solutions were determined in the copper reboiler of the rectifying column at four concentrations, each at four different steam pressures. Plots of heat flux against diol concentration and temperature difference were constructed, and, by transferring from one plot to another, a plot was obtained of the over-all coefficient of heat transfer against temperature difference at various diol concentrations. Representative results are given in Table IX. The tubes of the calandria had been used for 18 months at the time of the tests and hence these values should be applicable to commercial operation.

TABLE IX

OVER-ALL COEFFICIENT OF HEAT TRANSFER FROM STEAM TO BOILING DIOL-WATER SOLUTIONS
IN A CALANDRIA TYPE HEATING UNIT

Temperature difference, °F.	Weight per cent diol				
	0	20	40	60	80
	B.t.u. per hr. per sq. ft. per °F.				
30	306	273	225	—	—
50	360	305	255	205	175
70	375	300	250	215	175

DRYING

A portion of washed and pressed bran was air dried to obtain samples for analysis. Stripping column residue was dried on an atmospheric double drum drier with drums 6 in. in diam. and 10 in. long. Samples of the dried residue were then analyzed. The performance of the drum drier is given in Table X and the results of the analyses are given in Table XI, together with analyses of commercial residues.

TABLE X

PERFORMANCE OF LABORATORY ATMOSPHERIC DOUBLE DRUM DRIER

	Sample 1	Sample 2
Solids in feed, %	17.2	13.3
Feed rate, lb. per hr.	11.9	8.1
Drum speed, r.p.m.	3	2
Steam pressure, p.s.i. gauge	45	20
Feed rate, lb. per hr. per sq. ft. of drum surface	0.048	0.049
Lb. water evaporated per hr. per sq. ft. of drum surface	0.040	0.0425
Over-all heat transfer coefficient, B.t.u. per hr. per sq. ft. per °F.	0.6	1.1

TABLE XI

ANALYSES OF PILOT PLANT AND COMMERCIAL RESIDUES*

	Dried stripper residue		Dried screen solids	Distillers grains from rye	Brewers grains over 25% protein	Strained distillery slop**
	No. 1	No. 2				
Butanediol, %	1.27	1.58	0.53			
Moisture, %	8.42	11.8	10.7	7.2	7.5	10.0
Soluble solids, %	59.4	55.6	0.0			
Ash, %	11.7	13.5	1.65	3.9	3.5	6.6
Total nitrogen, %	5.59	6.02	1.21	3.7	4.24	4.91
Water soluble nitrogen, %	4.05	4.40	0.21			
Total P ₂ O ₅ , %	2.33	2.96	1.33	0.83	0.99	
Available P ₂ O ₅ , %	2.21	2.82	1.13			
Total K ₂ O, %	0.11	0.10	0.07	0.24	0.09	
Total CaO, %	5.4	5.5	0.74		0.16	
Crude protein, % N × 6.25	34.9	37.6	7.56	23.1	26.5	30.7
Fat, %	5.1	5.0	3.4	7.8	6.9	15.4
Fiber, %	2.0	2.3	27.0	10.9	14.6	4.4
Nitrogen free extract, %	37.9	29.8	49.5	47.1	41.0	32.9
Thiamine, p.p.m.	0.0		0.0			
Riboflavin, p.p.m.	1.64		1.3			
Nicotinic acid, p.p.m.	88		6.4			

* Thanks are due the Analytical Laboratory of the Division of Chemistry, National Research Council, to Dr. C. V. Marshall of the Department of Agriculture, and to Dr. Dyson Rose of the Division of Applied Biology, National Research Council, for analyses of the pilot plant residues. The analyses of the commercial residues were taken from Henry, W. A. and Morrison, F. B., *Feeds and Feeding*, 19th Edition, The Henry-Morrison Company, Ithaca, New York, 1928.

** Calculated to a 10% moisture basis.

The ash content of the stripper residue was high because it contained all the calcium carbonate added to the mash. The butanediol values shown represent most of the diol originally present in the wet residues since only a small amount was removed in the drying process. The diol content of the residues may be reduced by more efficient stripping of the stripper residue or by more complete washing of the bran prior to drying. Oral toxicity tests of 2,3-butanediol were performed by Dr. L. I. Pugsley of the Department of National Health and Welfare on adult male rats. The tests showed that the lethal dose for 50% mortality was 11.5 ml. per kilogram of body weight. No tests were made to determine whether the effects are cumulative.

No thiamine was present in any of the solids. The riboflavin content of the stripper residue represents approximately 100% and the nicotinic acid content about 50% of the totals originally present in the wheat, although the residue was only 30% of the weight of the wheat. The bran contained about 50% of the amount of riboflavin and 100% of the nicotinic acid usually present in wheat brans. Comparisons of the nitrogen, phosphorus, and potash contents of the dried stripper residue with commercial fertilizers indicate that this material is of little value for this purpose. Although of a higher quality than dried manures, it could not compete with ordinary fertilizers without being enriched with either phosphorus or potash. The dried bran is of even less value as a fertilizer.

The dried stripper residue appeared to have considerable possibilities as a livestock feed. It was higher in protein and minerals than any of the commercial residues but somewhat lower in fat and fiber content. The composition of strained distillery slops corresponded most closely to that of the stripper residue. The dried bran is of little value as a food except as roughage.

Quantitative Flow sheet

For the purposes of cost estimates a quantitative flow sheet with estimates of the size of equipment was necessary. The flow sheet and cost estimates were based on a plant with a capacity of 1000 bu. per day. The flow sheet, with weights and compositions, is shown in Fig. 4, and the cost estimates are given in the following section. The composition of the fermented mash calculated for a 15% mash, 90% fermentation efficiency of wheat containing 50% starch, and a diol to ethanol ratio of 1.50 has already been given.

Ethanol Recovery

The diol and ethanol recoveries shown on the flow sheet are the same as those obtained in the pilot plant since the same column height, feed rate, and reflux ratio could be used. The steam to the preheater is that required to heat the mash to the boiling point. The details of concentrating and purifying the high wine are not shown but the cost of this operation was included in the cost estimates. The column, preheater, and condenser could be constructed of copper, as is customary in the distillery industry.

Screening and Pressing

The material balance for the initial screening was calculated from the following values: total solids in slops, 6.61%; total solids in screenings, 13.5%; and ratio of insoluble solids to total solids in slops, 0.13. The screenings would then contain 9.73% of the diol and soluble solids and 21.5% of the total solids. If these screenings were pressed without washing, the diol loss would be 2.4% and diol content of the screenings on a dry basis would be 5.6%. Thus, washing would be required both to reduce the diol loss and to reduce the diol content of the dried bran.

If pressing is omitted, it is economical to supply wash water until the marginal diol recovery is such that the cost of evaporating the additional water equals the value of the diol recovered. Since washing does not change the ratio of diol to solids in the screen filtrate, adding wash water will affect only the evaporation. If the increase in fixed charges caused by the wash water is neglected, washing should be continued until the marginal weight of water required to recover one pound of diol is that given by the expression:

$$\frac{1000ae}{s},$$

where a is the value of diol in cents per pound, e is pounds of water evaporated per pound of steam, and s is the cost of steam in cents per 1000 lb. If a is 20, e , 1.70, and s , 25, washing should be continued until 1360 lb. of water is required to recover 1 lb. of diol. Adding water, however, decreases the diol recovered by pressing and it was found by trial calculations that a marginal diol recovery of 1 lb. per 750 lb. of water is a more economical recovery than 1 lb. per 1360 lb.

Fig. 4 shows a material balance for a washing with one equilibrium contact with an amount of water such that the marginal diol recovery is 1 lb. per 750 lb. of water. It was assumed that the total weight of screenings and the per cent insoluble solids would not change during washing. The material balance for pressing was calculated by taking the total solids concentration of the pressed bran to be 30.9%. The diol loss is 0.5% and the diol content of the bran on a dry basis is 1.33%.

Evaporation

It is believed that any feed arrangement in a multiple effect evaporator would be technically satisfactory, and cost alone would determine the choice of an arrangement. Blom *et al.* (4) suggested a quadruple effect evaporator with a feed order of 2, 3, 4, 1 and Othmer *et al.* (16) suggested an order of 3, 2, 1 for a triple effect evaporator. Each effect would be surmounted by a rectifying column to prevent diol from being lost in the vapor. The vapor-liquid equilibria data of the system *levo*-2,3-butanediol-water were reported by Knowlton (9) for pressures below and just slightly above atmospheric. Measurements at pressures ranging from 14.7 to 75 p.s.i. abs. were reported by Tomkins *et al.* (20).

Calculations for this operation for the quantitative flow sheet were based on a double effect evaporator with forward feed. Rough estimates were made of total materials and diol concentrations using over-all coefficients of heat transfer of 800 and 300 B.t.u. per hr. per sq. ft. per °F. It is expected that higher values than those obtained in the pilot plant kettle would be obtained with vertical tube evaporators. (The evaporation of screened distillery slops has been described by Herman *et al.* (8).) Approximate economical reflux ratios were calculated for the two rectifying columns, and the complete material distribution was then calculated by means of heat and material balances. From the initial and operating costs of this double effect evaporator it was estimated that the economical number of effects is 2.4.

Since both the distillate and syrup are acidic, an acid resistant material should be used in fabricating the evaporator bodies, columns, and piping. If lime or other alkali is not added to the filtrate, copper or copper base alloys would be satisfactory. If alkali is added, the syrup and distillate will contain free ammonia and most copper base alloys would be unsatisfactory. Stainless steel and monel would give least corrosion, but iron and steel might prove to be satisfactory if sufficient alkali were used. Standard iron pipe was satisfactory for handling cold filtrate in the pilot plant.

Whether or not the diol in the vapor from the final feed effect of a large scale evaporator would be recovered by rectification or returned to the syrup depends on economic factors. Forward, backward, or mixed feed could be used and the final column could be operated at one of a number of different pressures. The diol recovered could be mixed with the diol from a stripping-scrubbing operation, ethanol precipitation, or any other recovery step used to recover diol from syrup. Material distributions could be calculated by material balances with the aid of vapor-liquid equilibria data.

Stripping and Scrubbing

In commercial production, over-all continuous operation of a stripping column would be obtained by means of a storage tank between the evaporator and the stripping column, to allow the syrup to accumulate while the column was being cleaned. This would be cheaper than installing two stripping columns and operating one while the other was being cleaned but the operation would be more difficult. Since the cost of cleaning a stripping column would be very small the flooding time is not important in choosing commercial operating conditions. The most important factor is the size of the column, which is determined by the solids content of the syrup and the syrup and steam rates. For a plant of a given size the average solids throughput per day or hour is a constant; thus the column diameter will be smaller at higher solids concentrations for the same syrup mass velocity. The number of transfer units, column height, and column diameter were calculated for a feed rate of 160 lb. per hr. per sq. ft. and a steam rate of 610 lb. per hr. per sq. ft. at the three solids concentrations for which flooding times are given in Table III. The diol concentration of the syrup was calculated from the solids concentration and the ratio of diol to solids. The diol lost in the

residue was set at 80 lb. per day, and the diol concentration of the vapor at the top of the column was calculated from a material balance. The number of transfer units was then computed as described previously. The height of a transfer unit was taken as 4 ft. for all concentrations. When diol concentrations were calculated for a feed rate of 210 lb. per hr. per sq. ft. and a steam rate of 610 lb. per hr. per sq. ft., it was found that these conditions were inoperable for the recovery desired. Operation at a solids content of 23.6% required both a shorter and a smaller column than the lower concentrations. Since the packing is the main item in the cost of a packed column and since the cost of auxiliary equipment would be almost the same for all concentrations, this concentration would give the lowest initial cost. Neglecting the cost of cleaning, which would be small, the operating costs for the three solids concentrations would be almost equal. Thus, the highest of the three solids concentrations would give the lowest total cost.

A solids concentration of 23.6% and the above feed rates and assumptions were therefore used for the quantitative flow sheet and cost calculations. The equilibrium and the stripping and scrubbing column operating lines used for these calculations are shown in Fig. 3. The estimated dimensions of the two columns are: 5.75 ft. in diam. by 37 ft. high for the stripping column,

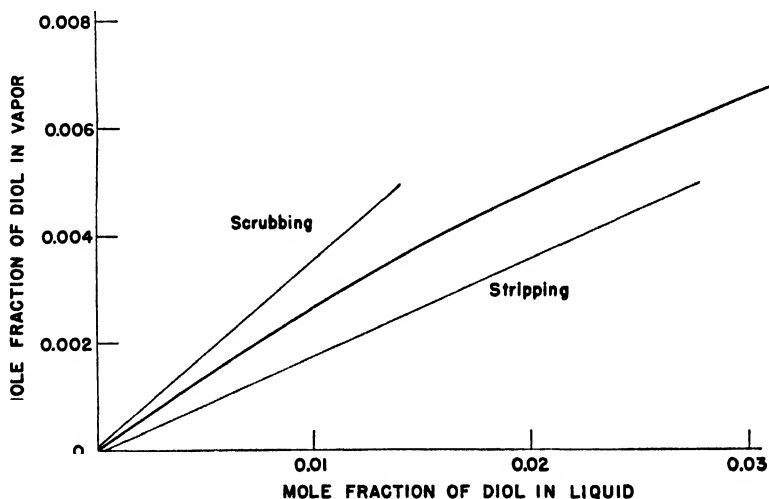


FIG. 3. Design diagram for stripping and scrubbing operations.

and the same diam. by 55 ft. high for the scrubbing column. The shells of the columns could be constructed of Ni-resist cast iron or steel but a stainless steel or monel clad steel would be better. If a bubble cap scrubbing column were used it should be constructed of an acid and ammonia resistant alloy such as stainless steel or monel.

From Fig. 4 it can be seen that the steam fed to the bottom of the stripping column is recovered at the top of the scrubbing column. The pressure of the recovered steam will be only slightly lower than the pressure of the inlet steam.

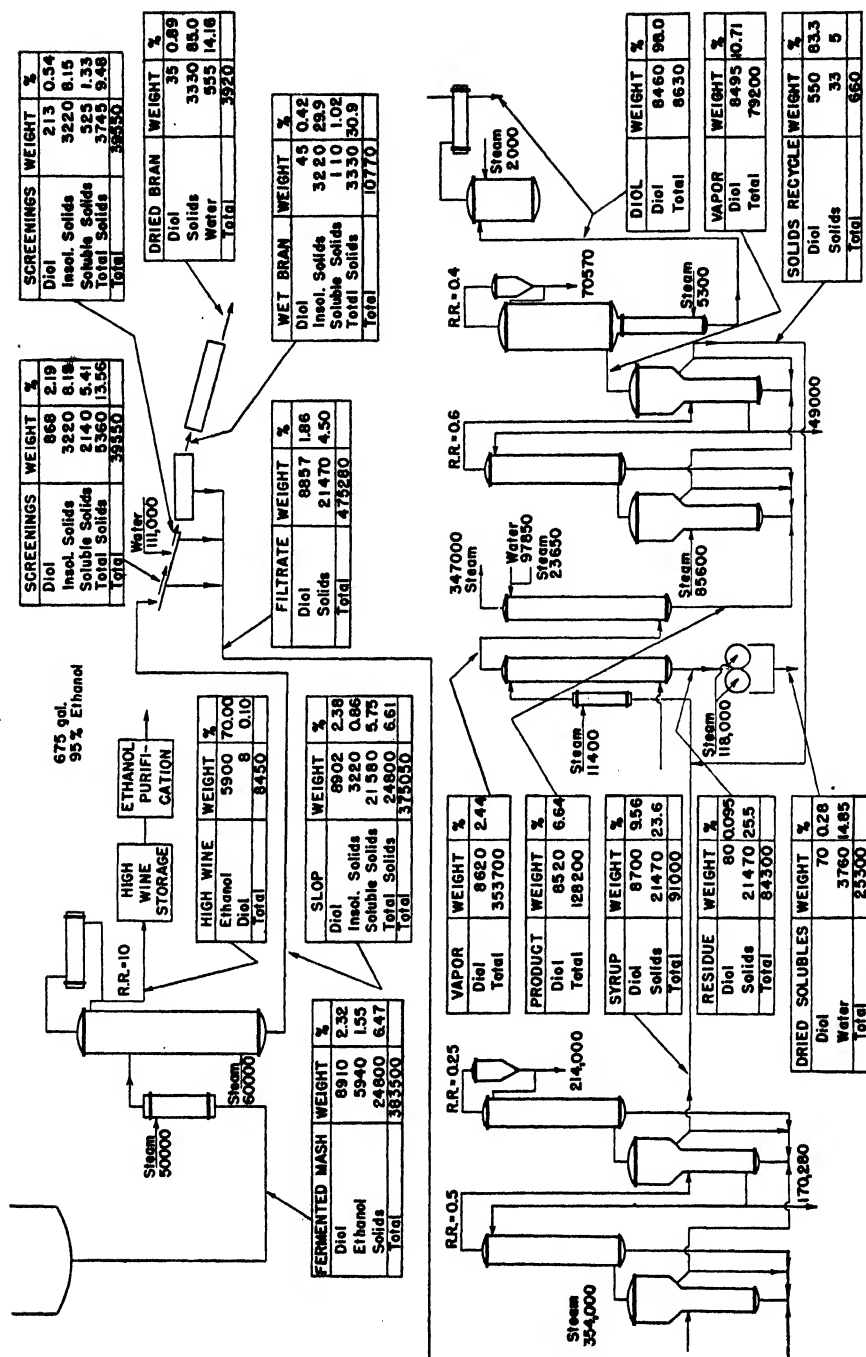


FIG. 4. Quantitative flow sheet for commercial production of levo-2,3-butanediol (basis: 1000 bu. of wheat per day).

The recovered steam could be used for the evaporators, or as shown by Callaham (5) a thermo-compressor could be used and the steam recycled. In both, the actual steam consumption of the stripping-scrubbing step is low.

Concentration and Purification

The most economical method to be used in commercial production for concentrating the scrubbing column product to 97–99% diol depends on the size of the plant. One method would be to feed the liquid scrubbing column product to a rectifying column operated at atmospheric pressure. The bottom product, containing 60 to 80% diol would then be vaporized, the vapor rectified at reduced pressure to 97–99% diol, and the liquid product would then be redistilled at reduced pressure. A second method would be to concentrate the scrubbing column product to 60–80% diol in a double effect evaporator with rectifying columns mounted on each effect. This partially concentrated product would then be vaporized, rectified, and redistilled. A third method would be to feed the vapors from the final effect of a multiple effect evaporator to a distillation column as is shown in Fig. 4. The first of these methods would have the lowest initial cost but the highest operating cost, while the second would have the highest initial cost and lowest operating cost. Thus, the first would be favored for a small plant and the second for a large plant. Approximate calculations showed that for a plant with a capacity of 1000 bu. per day the total costs of the three methods are almost equal. The third one, which is intermediate in both initial and operating costs, was chosen for illustrative purposes.

Initial approximations and methods of calculation similar to those used in computing the material distribution for the screen filtrate evaporator were used for this operation. Over-all coefficients of heat transfer of 800 and 400 B.t.u. per hr. per sq. ft. per °F. were assumed for the two effects. Since the scrubbing column product would contain a small amount of solids, they must be withdrawn from the second effect and recycled with the syrup. An estimate of the amount and composition of the recycled material is shown in Fig. 4 but it is not included in the stripping, scrubbing, and concentrating operations. If ion exchangers were used for purification they would be placed between the scrubbing column and the evaporator. If direct neutralization were used, sodium hydroxide would be added to the second effect of the evaporator. In either method a small amount of sodium hydroxide would be added to the final distillation evaporator.

Copper or copper base alloys could be used for the concentration equipment up to the point where sodium hydroxide is added. For the final stage of the concentration and the redistillation of the product the material of construction should be resistant to acids and ammonia. Lead and zinc are not satisfactory.

Cost Estimates

The pilot plant work has shown that recovery of *levo* 2,3-butanediol from whole wheat mashes fermented by *A. polymyxa* is technically feasible. The quantitative flow sheet shown in Fig. 4 was prepared for the purpose of cost

estimates and to illustrate the distribution of materials described in the experimental section. The data and assumptions used in computing the flow sheet have already been stated. In preparing cost estimates it was necessary, of course, to include mashing and fermenting operations. A plant with a capacity of 1000 bu. a day would require five cookers with a capacity of 1500 gal. each, four or five 500 gal. propagators and 10 fermenters with a fermenting capacity of 20,000 gal. each. The initial cost was estimated to be \$500,000.00 (1945), which is \$500.00 per daily bushel of wheat or \$304.00 per yearly ton of diol. Raw material, steam, water, power, labor, and products produced are given in Table XII. In addition to labor, the plant would require a management* staff of administrative and technical personnel and assistants. A management cost of \$105.00 per day was allowed in the estimate.

TABLE XII
RAW MATERIALS, ENERGY REQUIREMENTS, AND PRODUCTS
(Basis: 1000 bu. of wheat per day)

Raw materials	
Wheat	1000 bu.
Calcium carbonate	2500 lb.
Malt	300 lb.
Sodium hydroxide	1000 lb.
Turkey Red Oil	50 lb.
Energy and power	
Steam	750,000 lb.
Water	850,000 gal.
Electric power	3500 kwh.
Labor	300 man-hours
Products	
<i>levo</i> -2,3-butanediol	8460 lb.
Ethanol, 95%	675 gal.
Dried grains (14.16% water)	3920 lb.
Dried solubles (14.85% water)	25300 lb.

The selling price of butanediol in dollars per gallon is given by the expression.

$$S.P. = \frac{1}{846} (1000A + 7.5B + 35C + 300D - 1.96E - 12.65F - 6.75G + 16.67H + 684)$$

where A = Cost of wheat, dollars per bushel;

B = Cost of steam, cents per 1000 lb.;

C = Cost of power, cents per kwh.;

D = Cost of labor, dollars per man-hour;

E = Selling price of dried grains, dollars per ton;

F = Selling price of dried solubles, dollars per ton;

G = Selling price of 95% ethanol, cents per gal.;

H = Profit, % of initial cost (\$500,000).

The constant, 684, includes factors not given by the variables in the expression, and 846 is the final diol yield in imperial gallons per 1000 bu. A depreciation rate of 2% was assumed for the building (\$100,000) and 7% for the plant equipment.

With wheat at \$1.10 per bu., steam at 25¢ per 1000 lb., electric power at 1¢ per kwh., labor at \$1 per man-hour, dried bran and solubles at \$30 per ton, and 95% ethanol at 60¢ per gal. the cost of production of butanediol is \$1.73 per gal. or 17.30¢ per lb. The distribution of costs and credits at the conditions listed above is shown in Table XIII. With wheat at \$1.00, \$1.25, and \$1.50 per bu. and all other costs and prices as above, the cost of production of butanediol is 16.1, 19.1, and 22.1¢ per lb., respectively.

TABLE XIII

COST AND CREDIT DISTRIBUTION FOR PRODUCTION OF BUTANEDIOL

Distribution	Percent of total	Cents per imp. gal.
Costs		
Fixed costs	14.30	39.10
Wheat	47.70	130.10
Other raw materials	5.46	14.89
Steam	8.15	22.20
Wages	13.00	35.50
Other production costs	11.39	31.13
	100.00	272.83
Credits		
Butanediol	63.8	173.15
Ethanol	17.2	47.88
Dried solids	19.0	51.80
	100.0	272.83

C. T. Langford (10) has given the cost of *levo*-2,3-butanediol as 10.62¢ per lb. This is based on a plant with a capacity of 8,500 bu. per day, a diol yield of 9.86 lb. per bu., and a grain cost of 70¢ per bu. The initial cost of the plant is \$240 per yearly ton of diol. The higher yield is probably due to the assumption of a higher starch content of the grain. If a yield of 8.46 lb. per bu. and a grain cost of \$1.10 per bu. had been used in Langford's estimate, the cost of butanediol would have been 16.5¢ per lb. (The cost of production of the *meso*-isomer would be appreciably less than that of the *levo*- because a larger portion of the starch is converted to diol and a smaller portion to ethanol.)

Acknowledgments

The authors wish to acknowledge assistance given by Messrs. A. Traeff and E. D. Unger of Joseph E. Seagram and Sons in the design and initial operation of the pilot plant. Thanks are due Coulter Copper & Brass Co. Ltd., Toronto, for construction of most of the equipment and for handling

many of the sub-contracts. Mr. J. Cody and Mr. R. E. MacMorran and their staffs, of the Division of Mechanical Engineering, National Research Laboratories, erected and serviced the pilot plant. Dr. Dyson Rose and Mr. W. S. King of this Division assisted in directing the installation of the units and also in initial operations. Finally, thanks are due the operational and laboratory staff of the pilot plant.

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PRODUCTION AND PROPERTIES OF 2,3-BUTANEDIOL

XXIX. PILOT PLANT STUDIES ON FERMENTATION OF BARLEY BY *AEROBACILLUS POLYMYXA* AND RECOVERY OF THE PRODUCTS¹

BY R. V. TOMKINS,² D. S. SCOTT,² AND F. J. SIMPSON³

Abstract

Barley mashes were successfully fermented by *Aerobacillus polymyxa* on a pilot plant scale. In the laboratory a 12.5% mash appeared to be optimum but more concentrated mashes were efficiently fermented in the pilot plant. The hulls caused some mechanical difficulties, but these were overcome by eliminating right angle joints in the piping and by screening before recovery operations. Products were recovered by the same operations as for wheat. The lower raw material cost of barley resulted in an estimated reduction in the production cost of *levo*-2,3-butanediol of 7%, based on 1947 prices; or a reduction of 10%, based on a long-term average for 1908-1940.

Introduction

The fermentation of wheat by *Aerobacillus polymyxa* has been thoroughly investigated both in the laboratory and the pilot plant to determine the feasibility of producing *levo*-2,3-butanediol on a commercial scale. A cost estimate based on this work for a plant to process 1000 bu. per day of wheat (5) showed almost half the cost of production to be due to the cost of the basic raw material. It was therefore considered desirable to assess the possibility of using western feed barley, which is a good source of starch and somewhat cheaper than feed wheat, as the substrate for the fermentation.

Some average analyses of wheat and barley are compared in Table I. These data are from Henry and Morrison (4) with the exception of the starch values, which are from analyses made in the National Research Laboratories.

TABLE I
PER CENT COMPOSITION OF WHEAT AND BARLEY
(All values on a moisture-free basis)

Component	Wheat	Barley
Ash	2.1	3.0
Crude protein	13.8	12.7
Fiber	2.4	5.1
Fat	2.3	2.3
Starch	58.0	51.8

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Fermentation

Barley mashes of various concentrations were fermented in the laboratory before large scale tests were begun. The desired amounts of ground grain and water were slurried together with 1% calcium carbonate, and 300-ml. amounts were placed in 500 ml. Erlenmeyer flasks and sterilized for one hour at 120° C. These samples were inoculated with 5 ml. of a 24 hr. culture of a barley medium, using the strain (C42-3) of *Aerobacillus polymyxa* that had given consistently good results with wheat. The mashes were incubated for 72 hr. at 32° C. and then examined and analyzed for products.

A mash concentration of 12.5% barley gave the most efficient fermentation (Table II). Mashes of higher concentration were very thick and 'jelled' into a solid mass. Such mashes remained in the jelled state for 24 to 48 hr.

TABLE II

EFFECT OF BARLEY MASH CONCENTRATION ON YIELD AND FERMENTATION EFFICIENCY
(300-ml. fermentations at 32° C.)

Mash concentration, %	Yield, lb./bu. (48 lb.)		Diol-alcohol ratio	Efficiency, %
	Diol	Alcohol		
10	5.5	4.3	1.3	78
12.5	6.4	5.7	1.1	96
15	6.1	4.5	1.4	84
17.5	5.4	3.6	1.5	72
20	5.1	2.9	1.8	64

after inoculation, then they broke up and fermented at a rapid rate, as shown by the production of gas. When the mash concentration had been properly adjusted, no further difficulty was experienced in fermenting barley mashes in the laboratory.

The fermentation procedure followed in the pilot plant was the same as that developed for wheat (2). The grain was ground in an attrition-type mill, metered into a mixing barrel with the required amount of water, and the slurry pumped to the cooker. The mash was sterilized for two hours at 120° C., then blown to a sterile fermenter. After cooling, 25 lb. of separately sterilized calcium carbonate was added, and the mash inoculated with two liters of a 24 hr. culture similar to that described for the wheat fermentation (1), with barley replacing the wheat. The final volume of the mash averaged 450 gal. The fermenter was maintained at 32° C., with agitation during the first 24 hr. At 96 hr. the fermentation was considered complete.

During the fermentation, samples were taken at 24-hr. intervals. The course of the barley fermentation was found to be similar to that of the wheat, average values being: 70% complete at 48 hr., 80% at 72 hr., and 90% at 96 hr. The pH trend was also similar, dropping sharply from an initial pH of 6.5, to 5.5-5.7 in 24 hr. with a final pH at 96 hr. of 5.3-5.7.

A summary of the final yields and efficiencies is given in Table III. The diol-alcohol ratio and efficiencies (see (2) for method of calculation) for the

TABLE III

FERMENTATION YIELDS AND EFFICIENCIES OF BARLEY MASHES AFTER 96 HR. INCUBATION AT 32° C.

(440-gal. fermentations at 32° C.)

Mash conc., %	Yield, lb./bu. (48 lb.)		Diol-alcohol ratio	Efficiency*, %
	Diol	Alcohol		
7.5	5.6	5.1	1.1	85
11.5	7.0	3.6	1.9	84
12.1	5.9	4.3	1.4	81
13.1	6.5	4.8	1.4	90
14.0	6.9	5.0	1.4	94
14.2	6.6	4.3	1.4	87
14.5	5.9	4.1	1.4	80

* Based on 47.3% starch in the barley.

barley are of the same order as those for wheat mashes of the same concentration. As the efficiencies are based only on total products and starch content of the mash, they are directly comparable to similar figures for wheat fermentations (2). Efficient fermentations were obtained with higher mash concentrations in the pilot plant than in the laboratory.

Some difficulty was encountered in the pilot plant when attempts were made to slurry the ground barley in the equipment used for wheat. A large portion of the barley hulls passed through the attrition-type grinder practically intact, and plugged the lines wherever sudden changes in direction or abrupt constrictions occurred. By altering the pipe, barley mashes up to 14.5% were slurried without difficulty. In commercial practice, the use of streamline pipe up to the point of removal of the hulls, or a grinder that would completely comminute the hulls, would probably solve this difficulty.

Recovery of Products

The same operations used in the recovery of alcohol and butanediol from wheat mashes were used for the barley mashes, with only a minor change in sequence. The fermented wheat mashes were stripped of alcohol in a beer still, the slop screened, and the filtrate concentrated with rectification. When barley was used, it was necessary to screen the fermented mash as the first step in order to remove the hulls, i.e., the mash was taken directly to a vibrating screen from the fermenters, and the filtrate was then sent to the beer column for alcohol removal. The remaining steps of the recovery process were the same as those for wheat mashes (5).

The 100 mesh screen and press rolls used removed 15% of the total solids from a wheat mash, but 35% of the total solids from a barley mash. This resulted in a screen filtrate having a butanediol-solids ratio of about 0.5, as compared with 0.4 for wheat. The results of several screening runs are given in Table IV.

TABLE IV

EFFECT OF BARLEY MASH CONCENTRATION ON SOLIDS REMOVED BY SCREENING, AND DIOL-SOLIDS RATIO OF THE FILTRATE

Mash conc., %	Total solids, lb.	Screen and press solids, lb.	Filtrate solids, lb.	Solids removed, %	Filtrate, diol-solids ratio
7.5	83.8	32.2	51.6	36.6	0.511
12.1	193.3	60	133.3	31.0	0.565
13.1	215.0	73	142	34.0	0.502
14.2	251.1	92.6	158.5	37.0	0.564

The bran (or insoluble solids) fraction from the barley was, of course, larger than that from wheat. The syrup obtained on evaporation of the filtrate contained 30 to 40% more butanediol than a wheat syrup of the same solids content. This would result in a correspondingly smaller amount of syrup, with a consequent reduction in the size of the stripping and scrubbing equipment required. The higher butanediol concentration in the syrup would also allow a scrubber product of higher butanediol concentration, so that less water would have to be evaporated to produce the final product. Since the bran fraction is larger, the stripper residue obtained will be less from a barley syrup than that from a wheat syrup. Unfortunately, the savings mentioned above are small compared with other costs (*vide infra*).

The composition of the residues obtained in the wheat and barley fermentations are given in Table V. Protein and fiber contents are substantially the

TABLE V

COMPOSITION OF CRUDE FERMENTATION RESIDUES, %

Residue	Wheat	Barley
Bran or hulls		
Protein	7.6	7.5
Ash	1.7	4.0
Fat	2.9	0.6
Fiber	29.0	25.1
Stripper residue		
Protein	36.2	38.6
Ash	12.6	17.7
Fat	3.6	6.5
Fiber	2.2	1.6

same for the comparable products of each fermentation. The barley products contain considerably more ash. The evaluation of wheat residues as fertilizers or feeds given by Wheat *et al.* (5) appears to apply equally well to the barley residues.

Estimate of Costs

Various wheat and barley statistics based on the long-term average for the period 1908–1940 are given in Table VI. All data were taken from the Canada

TABLE VI
WHEAT AND BARLEY STATISTICS
(Based on average values, 1908–1940)

Cost and yield values	Wheat	Barley
Price, cents/bu.	87	51
Price, cents/lb.	1.47	1.06
Price, cents/lb. starch*	2.83	2.26
Yield, bu./acre	15.6	23.3
Yield, lb. starch/acre	487.0	526.0
Yield, dollars/acre	13.6	11.9

*Basis: Wheat, 52%; barley, 47% starch as received.

Year Book (3). On this basis, barley gives a higher yield of starch per acre than wheat, but the monetary return to the grower is less. Cost estimates based on the fermentation of wheat (5) showed that the raw material cost is about one-half of the total cost of butanediol. Therefore, the percentage reduction in the cost of butanediol would be one-half the percentage reduction in the cost of starch.

A comparison of the product yields of wheat and barley fermentations are given in Table VII and the comparative cost estimates based on current and

TABLE VII
COMPARISON OF YIELDS OF WHEAT AND BARLEY FERMENTATIONS
(Basis: 30 tons per day—1000 bu. wheat or 1250 bu. barley at 13.5% moisture)

Products	Wheat	Barley
Butanediol recovered, gal.	846	781
Alcohol recovered, gal. 95%	675	610
Bran or hulls, 13.5% moisture, tons	1.89	5.12
Residue, 13.5% moisture, tons	12.20	9.53
Total residues	14.09	14.65

TABLE VIII

COMPARISON OF COSTS OF WHEAT AND BARLEY FERMENTATIONS
(Basis: 30 tons per day—1000 bu. wheat or 1250 bu. barley at 13.5% moisture)

Production costs and credits	Wheat		Barley	
	Present	Long-term average	Present	Long-term average
<i>Costs</i>	\$	\$	\$	\$
Grain*	1270.00	870.00	1025.00	637.50
Utilities (steam, power, water)	265.00	265.00	261.00	261.00
Other costs (wages, fixed costs, etc.)	941.50	941.50	941.50	941.50
Total daily cost	2476.50	2076.50	2227.50	1840.50
<i>Credits</i>	\$	\$	\$	\$
Ethanol at \$0.60 per gal.	405.00	405.00	366.00	366.00
Residues at \$30.00 per ton	422.70	422.70	439.50	439.50
Butanediol	1648.80	1248.80	1422.00	1035.00
	¢	¢	¢	¢
Cost butanediol per lb.	19.5	14.8	18.2	13.3

* Wheat—present price, \$1.27 per bu.; long-term average, \$0.87 per bu. Barley—present price, \$0.82 per bu.; long-term average, \$0.51 per bu.

long-term average prices are given in Table VIII. All costs and credits have been taken from the figures given by Wheat *et al.* (5). These estimates show that at present Western Canadian prices (1947) a saving of 7.0% would result from the substitution of barley for wheat in the *Aerobacillus polymyxa* fermentation, and on the basis of long-term average grain prices a 10% cost reduction could be expected. As was previously mentioned, the use of barley also makes other savings possible.

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NONISOTHERMAL PRESSURE DROP FOR A GAS¹

BY NORMAN EPSTEIN² AND JOHN B. PHILLIPS³

Abstract

An equation for calculating the pressure drop in gas flow accompanied by large temperature change, derived from the differential form of the Bernoulli theorem combined with the heat transfer rate equation, was examined experimentally. Heating runs were made in the Reynolds number range 6000 to 15,000, for air flowing through a single horizontal $\frac{1}{4}$ in. standard steel pipe with steam jacket. The pressure drops calculated from the proposed equation were found to agree very closely with the observed experimental values. The method of evaluating pressure drop for turbulent nonisothermal flow by assuming isothermal conditions at a temperature midway between the surface temperature and the mean bulk temperature of the fluid, first developed by McAdams for certain oils, was also tested for a number of selected runs. This method was found to be as accurate as the previous one, and to have the advantage of being less cumbersome in application.

Introduction

The problem of fluid friction for isothermal flow in round pipes has been very thoroughly investigated as compared with that for nonisothermal flow. The friction factor f is defined (16) by the familiar differential form of Bernoulli's theorem:

$$dx + vdp + \frac{vdu}{g} + \frac{2fu^2dL}{Dg} = 0,$$

where the symbols have the meanings listed in the nomenclature. For streamline or viscous flow, the law established by Hagen (4) in 1839 and Poiseuille (11) in 1842 has been many times confirmed if the calming length were at least 30 diameters (13). In terms of the present symbols it is

$$f = \frac{16}{Re}.$$

For turbulent flow, the accepted friction factor plots for smooth tubes and clean commercial iron and steel pipes, respectively, are those of Drew, Koo, and McAdams (3), the results of an all-embracing literature survey. In the case of corroded or tuberculated commercial pipes, however, especially those

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of smaller diameter as in the present investigation, values of f are considerably greater than those read from the aforementioned plots (2, 7), and a roughness factor must be applied.

Recorded research on nonisothermal fluid friction has so far been restricted to liquids only, particularly oils. Available data (1, 5, 6, 18) all indicate that for a given value of the Reynolds number based on a viscosity evaluated at the mean bulk temperature of the oil, the friction factor during heating is less than in isothermal flow, while, for cooling, the friction factor is greater, especially when the flow is in the viscous region. These results have been reconciled with the isothermal friction factor plots by evaluating the viscosity at a temperature

$$t' = t + (t_s - t)/4$$

for streamline flow, and

$$t' = t + (t_s - t)/2$$

for turbulent flow (10). Another successful correlation, based on the same data as well as other data (14), involves multiplying the friction factor for nonisothermal flow by a correction ψ , where

$$\psi = 1.1 (\mu/\mu_s)^{0.25}$$

for viscous flow, and

$$\psi = 1.0 (\mu/\mu_s)^{0.14}$$

in the turbulent region (15). In a study of the cooling of water in a brass tube (12), it was found that nonisothermal friction factor data fall in line with isothermal data when the viscosity term in the Reynolds number is evaluated at the mean wall temperature. A complex triple integral expression (8, pp. 571-577) relating isothermal and nonisothermal pressure drop for viscous flow has been verified for water and an oil (9).

In the case of nonisothermal flow of gases, since the variation of viscosity with temperature is small as compared with that of liquids, the problem of finding the correct temperature at which to evaluate Re in order to use isothermal friction data is of minor consequence (6). But the compressible property of gases introduces the new problem of how to evaluate correctly the changing specific volume, which occurs explicitly in the pressure head term of Bernoulli's equation, and implicitly in the velocity head and Fanning friction terms. Where the specific volume does not vary greatly, the Bernoulli differential equation may be integrated with little error by using an average value of v (17). However, this is not applicable to cases where the variation of v is large.

A method of integrating the differential form of the Bernoulli equation by assuming that the pressure change is small compared with the temperature change was developed by J. H. Holden and W. Gauvin of McGill University in 1943, using simple thermodynamic relations. The present investigation was undertaken for the purpose of testing this formula within the lower turbulent range for the heating of air.

Formula Derivation

The energy balance for the flow of gases has been developed as follows (17). The differential form of Bernoulli's equation is given by

$$vdp + \frac{u du}{g} + \frac{2fu^2 dL}{Dg} = 0 \quad (1)$$

for a horizontal conduit.

Converting from local velocity u to average velocity V , since $V/v = G$, and $dV = Gdv$ for steady flow,

$$vdp + \frac{G^2 v dv}{g} + \frac{2fG^2 v^2 dL}{Dg} = 0.$$

Multiplying through by p/v ,

$$pdp + \frac{G^2 p dv}{g} + \frac{2fG^2 p v dL}{Dg} = 0.$$

Substituting the ideal gas law relation $p = NRT/v$,

$$pdp + \frac{G^2 NRT dv}{vg} + \frac{2fG^2 NRT dL}{Dg} = 0. \quad (2)$$

For isothermal flow, this equation can be integrated directly to the familiar form

$$\frac{p_1^2 - p_2^2}{2} = \frac{NRTG^2}{g} \left(\ln \frac{p_1}{p_2} + \frac{2fL}{D} \right). \quad (3)$$

For nonisothermal flow, Equation (2) is rearranged:

$$pdp + \frac{NRTG^2}{g} \cdot \frac{dv}{v} = - \frac{2NRTfG^2 dL}{Dg}.$$

Since the Reynolds number does not vary greatly, f may be considered constant, and an average value used. Holden and Gauvin considered that if the change in pressure is relatively small compared with the change in temperature, then dT/T may be substituted for dv/v , and this leads to an expression that could be integrated:

$$pdp + \frac{NRG^2 dT}{g} = - \frac{2NRTfG^2 dL}{Dg}.$$

In order to integrate this equation T must be expressed as a function of L . By a heat balance on a differential length dL ,

$$G\pi D^2 c dT/4 = h\pi D(t_s - T)dL,$$

or

$$\frac{dT}{t_s - T} = \frac{4h dL}{D G c}.$$

Integrating between $T = T_1$ at $L = 0$, and any value T and L ,

$$\ln \frac{t_s - T_1}{t_s - T} = \frac{4hL}{DGc} = \alpha L,$$

where α replaces $4h/DGc$.

Therefore
$$\frac{t_s - T_1}{t_s - T} = e^{\alpha L}$$

or
$$(t_s - T_1)e^{-\alpha L} = t_s - T.$$

Rearranging,
$$T = t_s - (t_s - T_1)e^{-\alpha L}.$$

Substituting in the energy balance,

$$pdp + \frac{NRG^2dT}{g} = -\frac{2NRfG^2}{Dg} \left[t_s - (t_s - T_1)e^{-\alpha L} \right] dL. \quad (4)$$

Integrating between the limits $p_1, T_1, 0$, and p_2, T_2, L ,

$$\begin{aligned} \frac{p_2^2 - p_1^2}{2} + \frac{NRG^2(T_2 - T_1)}{g} &= -\frac{2NRfG^2}{Dg} \left[t_s L + \frac{(t_s - T_1)e^{-\alpha L}}{\alpha} \right]_0^L \\ &= -\frac{2NRfG^2}{Dg} \left(t_s L + \frac{t_s - T_1}{\alpha e^{\alpha L}} - \frac{t_s - T_1}{\alpha} \right) \\ &= +\frac{2NRfG^2}{Dg} \left(\frac{t_s - T_1}{\alpha} - \frac{t_s - T_1}{\alpha e^{\alpha L}} - t_s L \right). \end{aligned}$$

For a rough pipe, f must be modified by the roughness factor X , and the final expression becomes

$$\frac{p_2^2 - p_1^2}{2} + \frac{NRG^2(T_2 - T_1)}{g} = \frac{2NRfXG^2}{Dg} \left(\frac{t_s - T_1}{\alpha} - \frac{t_s - T_1}{\alpha e^{\alpha L}} - t_s L \right). \quad (5)$$

Description of Apparatus

A diagrammatic sketch of the apparatus used in this investigation is shown in Fig. 1. A steady flow of air was provided by means of a rotary compressor, belt-driven by a $\frac{1}{4}$ hp. motor. The air rate was controlled by means of a by-pass valve to the atmosphere and was measured by an orifice. The orifice drop was read on a water manometer and the orifice upstream pressure on a mercury manometer. The steam pressure was regulated by means of a globe valve and measured on a Bourdon gauge. A calming length of 50 diameters preceded the heating section ($L = 5.0$ ft.), which consisted of a $\frac{1}{4}$ in. standard steel pipe ($D = 0.0303$ ft.) inside a $\frac{3}{4}$ in. standard steel steam jacket, with magnesia-asbestos ("Aircell") lagging ($\frac{1}{8}$ in. thick) on the outside. Thermometers were placed at the inlet and outlet of the heating section, and the pressure drop across this section was read on a mercury manometer.

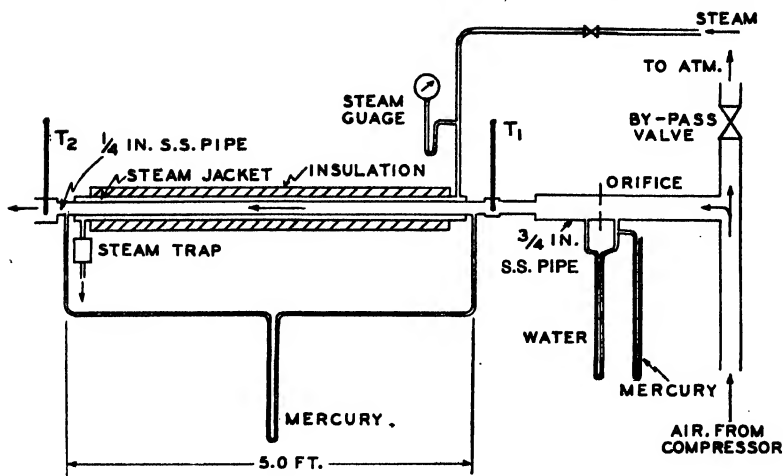


FIG. 1.

Experimental Procedure

In order to determine the roughness factor and its variation with mass velocity, a set of 10 isothermal trials were made initially throughout the entire velocity range of the apparatus.

Four sets of 10 heating runs each were then made at steam pressures of 5, 10, 15, and 20 p.s.i. gauge, respectively. Each run was carried on for 20 min. after ensuring that thermal equilibrium had been reached, and readings of orifice drop and pressure, inlet, and outlet temperatures, and pressure drop, were recorded at five-minute intervals.

The mean values of the above readings for each run were used in Equation (5) to calculate the pressure drop. The temperature corresponding to saturated steam at the recorded steam pressure was taken as the inside surface temperature (t_s) of the conduit, as calculations showed that the air film was controlling. The calculated and observed pressure drops for the 40 runs are given in Table I.

TABLE I
COMPARISON OF CALCULATED AND OBSERVED PRESSURE DROPS

t_s , ° F. abs.	Run No.	G , lb./ (sec.) (ft.) ²	$\Delta p_{calc.}$ cm. Hg	$\Delta p_{obs.}$ cm. Hg	Dev'n., %
687.1	1	2.92	1.36	1.44	-5.55
	2	3.65	2.08	2.17	-4.15
	3	4.05	2.55	2.59	-1.55
	4	4.64	3.32	3.34	-0.60
	5	4.91	3.65	3.72	-1.88
	6	5.30	4.25	4.29	-0.93
	7	5.60	4.66	4.67	-0.21
	8	5.97	5.26	5.32	-1.13
	9	6.25	5.75	5.70	+0.87
	10	6.40	6.00	5.98	+0.33

TABLE I—*Concluded*COMPARISON OF CALCULATED AND OBSERVED PRESSURE DROPS—*Concluded*

t_h , ° F. abs.	Run No.	G , lb./ (sec.) (ft.) ²	$\Delta p_{calc.}$ cm. Hg	$\Delta p_{obs.}$ cm. Hg	Dev'n., %
699.4	11	2.74	1.23	1.30	-5.38
	12	4.08	2.60	2.71	-4.05
	13	4.46	3.13	3.15	-0.63
	14	5.10	3.95	4.01	-1.49
	15	5.20	4.14	4.12	+0.48
	16	5.71	4.99	5.04	-0.99
	17	5.94	5.26	5.31	-0.94
	18	6.14	5.63	5.66	-0.53
	19	6.26	5.94	5.91	+0.51
	20	6.45	6.20	6.08	+1.97
709.8	21	2.96	1.43	1.51	-5.30
	22	3.80	2.30	2.44	-5.98
	23	3.95	2.45	2.60	-5.77
	24	4.45	3.12	3.21	-2.80
	25	4.91	3.74	3.87	-3.36
	26	5.36	4.45	4.57	-2.62
	27	5.75	5.05	5.16	-2.13
	28	6.06	5.56	5.61	-0.89
	29	6.28	5.78	6.00	-3.67
	30	6.51	6.37	6.37	0.00
718.8	31	2.86	1.34	1.36	-1.47
	32	3.51	1.99	2.02	-1.48
	33	3.95	2.52	2.49	+1.20
	34	4.51	3.22	3.24	-0.62
	35	4.91	3.76	3.82	-1.57
	36	5.42	4.58	4.62	-0.87
	37	5.53	4.66	4.79	-2.71
	38	5.91	5.33	5.43	-1.84
	39	6.08	5.64	5.70	-1.05
	40	6.43	6.25	6.29	-0.64

Discussion

The results indicate substantial agreement between calculated and observed pressure drops for the entire range of velocity and steam pressure used in the investigation. Although the deviation range of -6% to +2% is within the possible experimental error, with the percentage deviations in general numerically decreasing with increase in manometer readings as would be expected, the preponderance of negative over positive deviations may not be merely a coincidence, and there were no apparent apparatus defects to account for it. The probable explanation lies in the fact that the calculations for these runs were made using a friction factor based on the mean air temperature, rather than a mean of the friction factors at the inlet and outlet of the heating section. The latter procedure would have resulted in a slightly higher value of f in each case, hence a slightly higher calculated pressure drop, and therefore a slightly higher (algebraically, not numerically) deviation. This contention was actually verified for a few sample runs. There would thus have been a more symmetrical distribution of positive and negative errors.

It should be noted that, from the derivation of Equation (5), this relation is applicable only when the pressure change is relatively small compared with the temperature change, and this disparity is often the case in industrial practice, e.g., in air heaters and coolers, gas preheaters, etc. Although the present experiment has verified this equation only for the heating of air in the lower turbulent region ($Re = 6000$ to $15,000$), there appears to be nothing in the derivation that would preclude its applicability to the heating or cooling of any reasonably "ideal" gas in either the viscous flow or higher turbulent ranges, if the above condition is assumed to hold. However, it is not valid to make such a generalization without further experimentation.

It was deemed of interest to calculate the pressure drop for a few of the runs in this investigation by means of the familiar relation (Equation (3)) for isothermal pressure drop for a gas. Since in the present case the pressure change is relatively small, and f must be modified by the roughness factor X , the above equation reduces to

$$\frac{p_1^2 - p_2^2}{2} = \frac{2NRt'G^2fLX}{gD},$$

where $t' = t + (t_s - t)/2$, and f is evaluated at t' . The runs selected for this calculation were those at the lowest and highest mass velocities for each of the four steam pressures. The results are tabulated in Table II.

TABLE II
EVALUATION OF DATA USING "ISOTHERMAL" EQUATION 3

t_s , ° F. abs.	Run No.	G , lb./ (sec.) (ft.) ²	t' ° F. abs.	$\Delta p_{calc.}$ cm. Hg	$\Delta p_{obs.}$ cm. Hg	% Dev'n. Eq'n. (3)	% Dev'n. Eq'n. (5)
687.1	1	2.92	646.0	1.41	1.44	-2.08	-5.55
	10	6.40	649.5	6.10	5.98	+2.01	+0.33
699.4	11	2.74	653.6	1.27	1.30	-2.31	-5.38
	20	6.45	656.8	6.30	6.08	+3.62	+1.97
709.8	21	2.96	661.0	1.48	1.51	-1.99	-5.30
	30	6.51	664.3	6.49	6.37	+1.88	0.00
718.8	31	2.86	668.8	1.40	1.36	+2.86	-1.47
	40	6.43	669.5	6.41	6.29	+1.91	-0.64

The calculated results are therefore generally as accurate as those obtained using the much more complex relation in Equation (5). This semiempirical method seemingly would be more useful in practice, at least for the lower turbulent range.

The fact that the deviations using Equation (3) are consistently greater algebraically than the corresponding deviations using Equation (5), and that there is a more symmetrical distribution of positive and negative errors in

the case of the former, supports the contention that the uneven distribution of deviations using the latter formula is not due to divergence of the actual apparatus from an ideal system.

Conclusions

Equation (5), developed by Holden and Gauvin, successfully predicts, with reasonable accuracy, the pressure drop for the flow of a gas in a horizontal pipe accompanied by a large temperature change, within the lower turbulent region ($Re = 6000$ to $15,000$).

The method of evaluating data for turbulent nonisothermal runs by assuming that these runs occur isothermally at a temperature midway between the surface temperature and the mean bulk temperature of the fluid, a method first developed by McAdams for certain oils, is as accurate as the method of Holden and Gauvin in predicting nonisothermal pressure drop of a gas flowing in a horizontal pipe, and has the advantage for industrial design purposes of being much less cumbersome.

Definition of Symbols

c = heat capacity of gas, B.t.u./ $(lb.)$ $(^{\circ}F.)$,

D = inside diameter of conduit, ft.,

f = friction factor in Fanning equation, dimensionless,

G = mass velocity of gas, lb./ $(sec.)$ $(ft.)^2$,

g = acceleration due to gravity, 32.2 ft./ $sec.^2$,

h = gas film coefficient of heat transfer obtained from a heat balance on the heating section, B.t.u./ $(sec.)$ $(ft.)^2$ $(^{\circ}F. \text{ abs.})$,

L = heating (or cooling) length of conduit, ft.,

N = reciprocal of molecular weight of gas, lb-moles/lb.,

p = fluid pressure, lb./ $ft.^2$,

p_1 = inlet pressure of gas, lb./ $ft.^2$,

p_2 = outlet pressure of gas, lb./ $ft.^2$,

$\Delta p_{calc.}$ = calculated pressure drop, cm. Hg.

$$= \frac{(p_1 - p_2) 76}{(144) (14.7)}$$

$\Delta p_{obs.}$ = observed pressure drop, cm. Hg.,

p_s = steam gauge pressure, lb./ $in.^2$,

R = ideal gas law constant, 1543 ft.-lb./ (lb-moles) ($^{\circ}$ F. abs.),

Re = Reynolds number, dimensionless, $= DG/0.000672 \mu$,

T = gas temperature, ($^{\circ}$ F. abs.),

T_1 = inlet temperature of gas, ($^{\circ}$ F. abs.),

T_2 = outlet temperature of gas, ($^{\circ}$ F. abs.),

t = mean bulk temperature of fluid, ($^{\circ}$ F. abs.),

t_s = surface temperature, ($^{\circ}$ F. abs.),

t' = $t + (t_s - t)/4$ for Re below 2100, ($^{\circ}$ F. abs.),

= $t + (t_s - t)/2$ for Re above 2100, ($^{\circ}$ F. abs.),

u = local velocity of fluid, ft./sec.,

V = average velocity of fluid, ft./sec.,

v = specific volume of fluid, ft.³/lb.,

X = roughness factor, dimensionless,

$$= \frac{\Delta p_{obs.}}{\Delta p_{theor.}}$$

x = height of conduit above arbitrary datum, ft.,

$\alpha = 4h/DGc$, ft.⁻¹

μ = viscosity of fluid at mean bulk temperature, centipoises,

μ_s = viscosity of fluid at surface temperature, centipoises.

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THE DETERMINATION OF THE EFFICIENCY OF A HYDRAULIC TURBINE BY A CALORIMETRIC METHOD¹

BY JOHN KATZMAN

Abstract

Western Electric bead type thermistors were used to determine the difference in temperature of the water between the headrace and tailrace of a hydraulic turbine at different loads on the turbine. From this temperature difference the maximum efficiency of the turbine was determined to be 92% and the unit flow of water in cubic feet per second was calculated.

Introduction

The calorimetric method for the determination of the efficiency of a hydraulic turbine was first developed in Europe (1), but only to a small extent. The temperature of water is increased by approximately $\frac{h}{778}^{\circ}\text{F.}$ when the water falls through a height of h feet. When this water passes through a hydraulic turbine at the lower level, the amount of energy taken from the water will show as a decrease in the temperature of the water; this decrease will depend upon the load on the turbine. The difference of the temperature of the water at the headrace and at the tailrace was obtained by means of thermistors.

This problem was brought to the attention of the author by the Shawinigan Water and Power Company. The measurements were made at the Shawinigan Water and Power Company powerhouse at Grand'Mère, Quebec, Canada.

Experimental

Two Western Electric bead type thermistors whose resistance at the ice point differed by only 0.6% were chosen from a group of eight. These thermistors were chosen because the measurements were made when the temperature of the water was 32° F. The thermistors were fixed by means of paraffin wax in brass tubes with small copper tips, Fig. 1. A small amount of mercury was placed at the bottom of the tip for better thermal contact. The tubes were fitted with 1½ in. brass unions with which the unit was attached to the supporting pipes that held them in place in the water.

Each thermistor was connected as one arm of a Wheatstone bridge, Fig. 2. The other two arms were respectively, a 10,000 ohm Leeds & Northrup "unmounted resistor" and a similar one of 9500 ohms connected to a Leeds & Northrup decade box of 999.9 ohms. A galvanometer (sensitivity, 0.26 $\mu\text{v.}$ per mm. at one meter) was used as a null point instrument. Six volts was impressed on the bridge. The galvanometer was mounted on a shock proof support.

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To calibrate the bridge the thermistors were placed in a vessel of two compartments, Fig. 3. Each compartment measured $2 \times 2 \times 2$ ft. and was filled with 200 lb. of crushed ice that was intimately mixed with water. Both

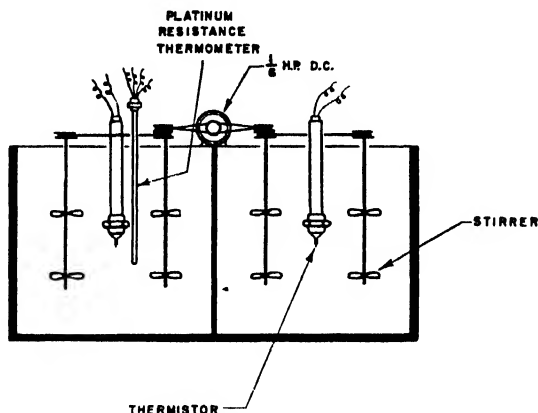


FIG. 3. Calibration baths.

thermistors were placed in one compartment and a bridge balance obtained. The thermistors were then placed separately in the ice baths and a platinum resistance thermometer was fixed beside one of the thermistors. Small quantities of sodium chloride were added to the ice-water mixture in which the resistance thermometer was placed. It was thus possible to obtain a bath whose temperature could be varied by small amounts. For each change in temperature by the one bath the bridge was balanced. The change in resistance necessary to balance the bridge was plotted against the change in temperature, Fig. 4.

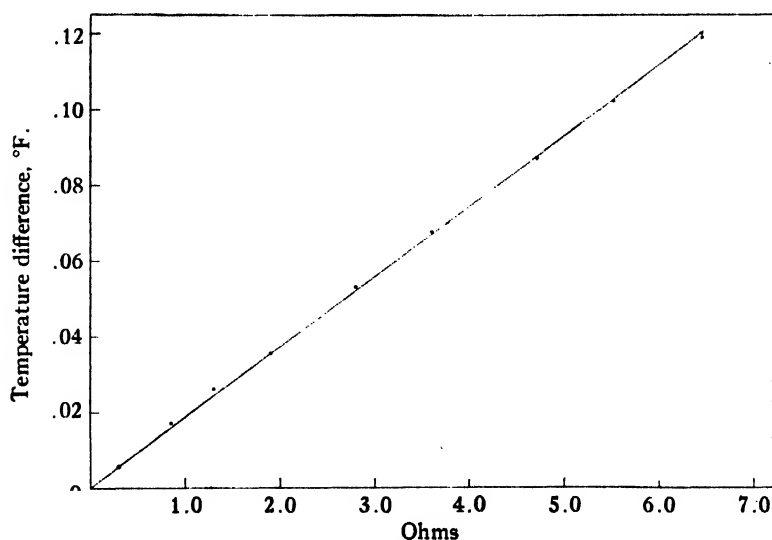


FIG. 4. Calibration curve of the Wheatstone bridge arrangement.

Tests

The No. 2 unit of the nine units at the powerhouse at Grand'Mère, Quebec, was chosen for test. All tests were made on Sundays because only then could the load on the turbine be varied at will and the unit could be put on independent hand control.

Both thermistors were lowered into the water of the headrace at the emergency gate opening and a balance on the bridge was obtained; this value was used as the zero. Then one thermistor was placed in position in the headrace and the other in the tailrace. The thermistor at the headrace was moved up and down for a distance of 20 ft. to determine whether the temperature of the water was uniform with depth. No change in temperature with depth was found. The same held for the tailrace. Temperature differences were measured for various gate openings, and at the same time readings of the turbine output and head of water were obtained from the control room.

Results

The results obtained are shown in Table I. Examination of the divided differences of the temperature difference indicated that, apart from random fluctuations, the relation of the temperature difference to the turbine output over the range studied could be adequately represented by a parabolic equation.

TABLE I

Temperature difference, ° F.	Turbine output, megawatts	Gate opening, %	Operating head, ft.	Temperature difference, ° F.	Turbine output, megawatts	Gate opening, %	Operating head, ft.
0.104	1.0	22.5	84.2	0.030	11.8	55.0	84.2
0.087	1.2	22.5	85.4	0.017	12.2	57.5	84.1
0.082	1.3	25.0	85.4	0.015	12.3	55.0	85.3
0.087	2.0	25.0	84.3	0.012	12.6	57.5	85.1
0.066	3.0	27.5	84.5	0.017	12.8	60.0	82.9
0.052	3.4	27.5	85.3	0.012	13.4	60.0	85.4
0.059	4.0	30.0	84.3	0.014	14.0	62.5	85.2
0.057	4.2	30.0	85.5	0.007	15.0	65.0	85.4
0.054	4.8	32.5	84.4	0.008	15.8	67.5	84.0
0.042	5.2	32.5	85.3	0.007	15.8	67.5	85.1
0.049	5.8	35.0	84.2	0.005	15.8	70.0	85.1
0.042	6.0	35.0	85.4	0.009	16.8	72.5	85.1
0.042	6.6	37.5	84.2	0.005	17.2	75.0	85.4
0.025	6.8	37.5	85.2	0.009	17.6	77.5	85.1
0.037	7.6	40.0	84.2	0.010	17.6	80.0	83.1
0.027	7.8	40.0	85.4	0.007	17.8	80.0	85.3
0.032	8.0	42.5	84.1	0.010	17.8	82.5	83.9
0.020	8.6	42.5	85.1	0.010	18.0	82.5	85.1
0.030	9.0	45.0	84.2	0.012	18.0	85.0	83.9
0.018	9.4	45.0	85.4	0.010	18.2	87.5	83.9
0.023	9.8	47.5	84.1	0.010	18.2	91.25	83.9
0.015	9.8	47.5	85.1	0.009	18.3	85.0	85.3
0.027	10.6	50.0	84.2	0.012	18.3	87.5	85.0
0.022	10.8	50.0	85.4	0.014	18.3	90.0	85.2
0.025	11.2	52.5	84.1	0.015	18.3	91.25	85.1
0.020	11.4	52.5	85.1	—	—	—	—

The parameters of such an equation were determined by the method of Least Squares by Mr. B. I. Wallace, Division of Biology, National Research Council of Canada. It was found that

$$t = 0.0999 - 0.0115x + 0.000362x^2, \quad (1)$$

where t is the temperature difference in degrees Fahrenheit and x is the turbine output in megawatts. The plot of this equation is shown in Fig. 5.

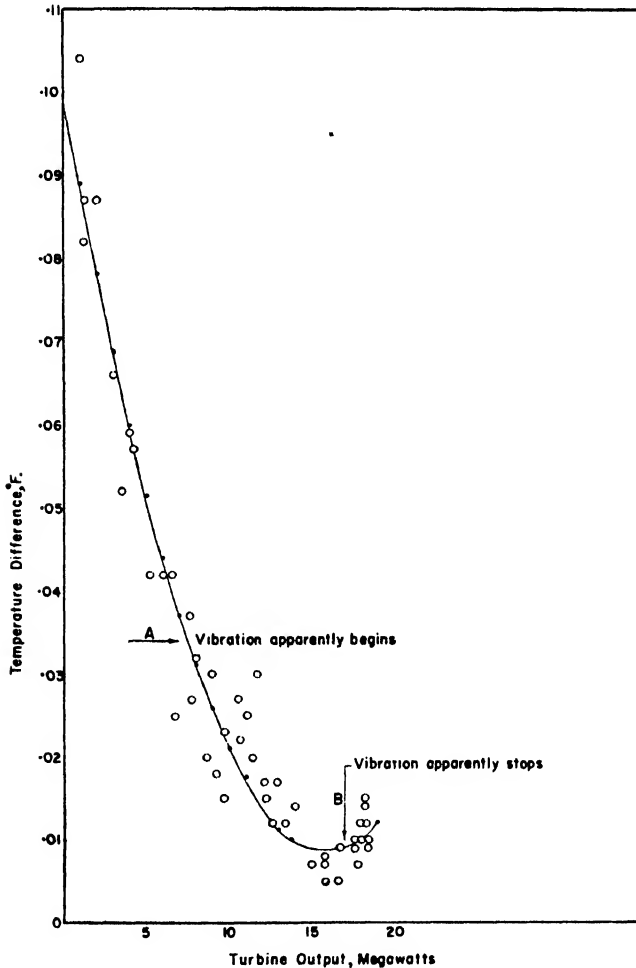


FIG. 5. Turbine efficiency curve.

The maximum efficiency is obtained when $\frac{dt}{dx} = 0$,

$$\frac{dt}{dx} = -0.0115 + 0.000724x$$

$$\therefore x \text{ max.} = 15,290 \text{ kw.}$$

that is, at a gate opening of 65%, Fig. 7, *B*. Substituting this value in Equation (1), $t = 0.0085^\circ \text{F.}$, and hence the maximum turbine efficiency is 92%.

The flow of water through a turbine can be determined if the temperature difference, the height of water, and turbine output are known.

Let P = horsepower obtainable for a height of water, h ft.,

p = turbine output, horsepower,

f = flow of water, c.f.s.,

t = temperature difference, $^\circ \text{F.}$ (measured).

$$\text{Then } P = \frac{fh \times 62.4}{550} = \frac{fh}{8.8}.$$

The temperature difference measured will be the temperature difference $\frac{h}{778}$ minus the loss in temperature difference caused by the turbine output.

$$\text{i.e., } t = \frac{h}{778} \left(1 - \frac{p}{P} \right)$$

$$\text{But } P = \frac{fh}{8.8},$$

$$\therefore f = \frac{p}{0.1136h - 88.4t} \quad (2)$$

If the turbine output is measured in horsepower, Equation (1) becomes

$$t = 0.0999 - (0.858 \times 10^{-8}) p + (0.2015 \times 10^{-9}) p^2. \quad (3)$$

From Equation (2)

$$t = \frac{1}{88.4} \left(0.1136h - \frac{p}{f} \right).$$

Substituting this value for t in Equation (3) and putting $h = 84.7$, we obtain,

$$\frac{1}{f} = \frac{0.792}{p} + 0.0007585 - (17.813 \times 10^{-9}) p. \quad (4)$$

The plot of this equation is shown in Fig. 6, and the calculated values in Table II.

The most efficient flow is at 1900 c.f.s.

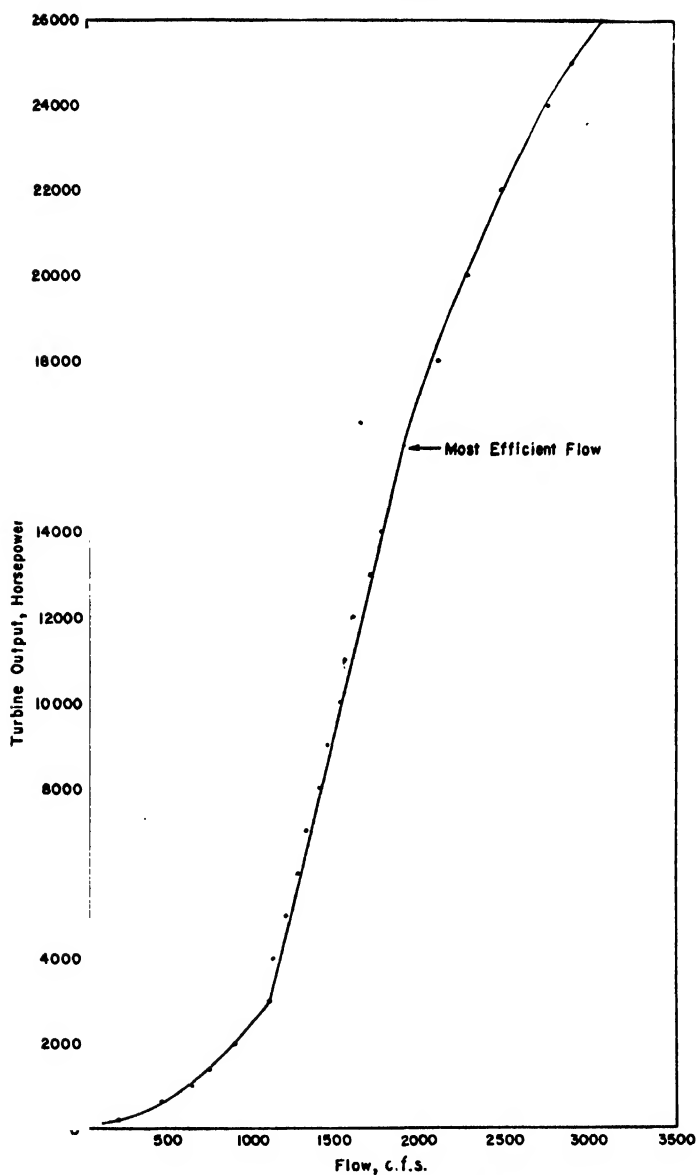


FIG. 6. Flow of water through the turbine in cubic feet per second at various loads on the turbine.

Three curves are shown in Fig. 7 that are of interest. Curve *A* is the plot of the gate opening against the temperature difference in degrees Fahrenheit, Curve *B* is of the gate opening against the turbine output in horsepower, and Curve *C* is of the gate opening against calculated flow in cubic feet per second. The variation in efficiency of the unit as determined by this method is shown by Curve *A*. The efficiency increases rapidly to a gate opening of about 50%, then not so rapidly to a maximum efficiency at a gate opening of 65%, and

TABLE II
CALCULATED UNIT DISCHARGE IN CUBIC FEET PER SECOND FOR
DIFFERENT LOADS ON THE TURBINE

Turbine output, hp.	Unit discharge, c.f.s.	Turbine output, hp.	Unit discharge, c.f.s.
200	212	10000	1516
600	483	11000	1544
1000	652	12000	1604
1400	769	13000	1701
2000	894	14000	1768
3000	1104	16000	1912
4000	1129	18000	2100
5000	1207	20000	2263
6000	1277	22000	2483
7000	1339	24000	2747
8000	1399	26000	3079
9000	1457		

then drops off slowly. Curve *B* is the plot obtained from the figures supplied by the powerhouse operator and it indicates maximum efficiency at a gate opening of about 70%. The values represented by dots of Curve *C* were obtained from Equation (4), the crosses representing the values obtained from Equation (2) when the temperature and turbine output are averaged for each gate opening, Table III.

TABLE III

TEMPERATURE DIFFERENCE AND TURBINE OUTPUT AVERAGED FOR EACH SETTING OF THE GATE
OPENING, FULL GATE = 100%; UNIT DISCHARGE OBTAINED FROM FIG. 8

Gate opening, %	Temperature difference, ° F.	Turbine output		Unit discharge, c.f.s.
		Megawatts	Horsepower	
22.5	0.096	1.1	1475	780
25.0	0.085	1.65	2211	950
27.5	0.059	3.2	4288	1175
30.0	0.058	4.1	5494	1250
32.5	0.048	5.0	6700	1325
35.0	0.046	5.9	7906	1400
37.5	0.034	6.7	8978	1460
40.0	0.032	7.7	10318	1550
42.5	0.026	8.3	11122	1 00
45.0	0.024	9.2	12328	1675
47.5	0.019	9.8	13132	1725
50.0	0.025	10.7	14418	1800
52.5	0.023	11.3	15142	1850
55.0	0.023	12.05	16147	1900
57.5	0.015	12.4	16616	1950
60.0	0.015	13.1	17554	2025
62.5	0.014	14.0	18760	2125
65.0	0.007	15.0	20100	2275
67.5	0.008	15.8	21172	2375
70.0	0.005	15.8	21172	2375
72.5	0.009	16.8	22512	2550
75.0	0.005	17.2	23048	2625
77.5	0.009	17.6	23584	2700
80.0	0.009	17.7	23718	2725
82.5	0.010	17.9	24016	2750
85.0	0.011	18.15	24321	2800
87.5	0.011	18.25	24455	2830
90.0	0.014	18.3	24522	2850

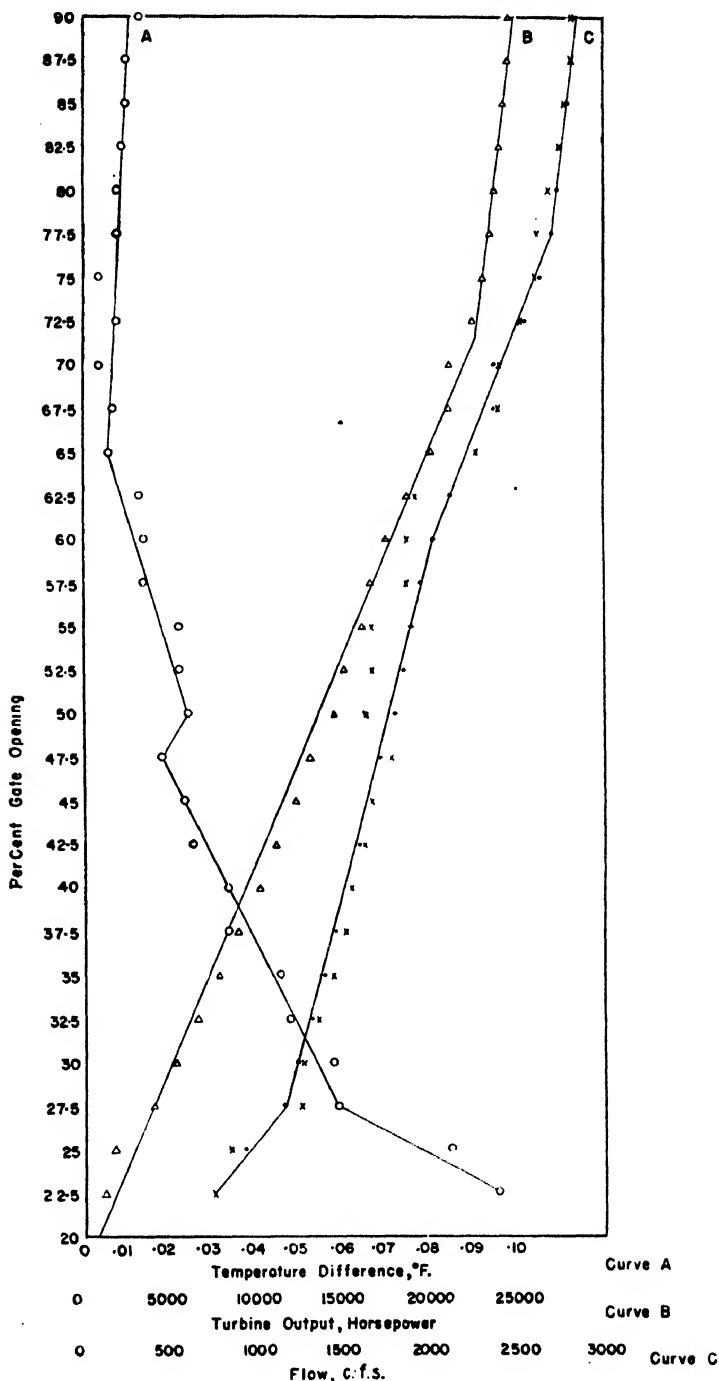


FIG. 7. Effect of gate opening on the temperature difference between the headrace and the tailrace (Curve A), the turbine output (Curve B), the flow of water through the turbine (Curve C).

It was noted that vibration of the power unit would begin at a gate opening of about 40%, increase to a maximum at about 55%, and then decrease until it could not be felt at about 70%. This vibration would cause fluctuations in the temperature of the water at the tailrace and is shown by the scatter of the values of Fig. 5 between the points marked *A* and *B*, and also by the crosses of Curve *C*, Fig. 7.

Acknowledgments

The author wishes to thank Mr. C. St. Jacques of the Physics Division, National Research Council of Canada, for the manner in which he assembled the apparatus and his assistance at the time of the tests, and Mr. W. R. McLeay, superintendent of the powerhouse for his keen co-operation.

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CANADIAN AERIAL MAGNETIC SURVEYS (M.A.D.)¹

BY RALPH BAILEY

Abstract

Tests concluded with an airborne magnetic detector measuring the earth's total field indicate a high degree of accuracy and speed for reconnaissance work over large areas. Cheapness of operation and freedom from small local anomalies make this a valuable tool for geophysical prospecting.

Introduction

For many years the measurement of magnetic anomalies in the terrestrial field has been a valuable method in geological studies and mineral location. To be able to map field variations rapidly by means of airborne equipment is an important advance in the application of geophysics to prospecting. This is now possible as a result of an intensive effort during the war to develop an airborne magnetic detector for submarine detection.

The purpose of this report is to describe the use of this instrument for studying magnetic contours over areas known to contain magnetic minerals, and the method by which these data may be presented so that they may be useful to those familiar with the interpretation of magnetic maps in relation to the geology of the area.

Many types of instruments depending on magnetic field variations were tried for detecting purposes during the war. Co-operation between the allied research laboratories was always possible and parallel development was carried out to meet specific requirements of the different armed services. Several types of magnetometers were made in the National Research Laboratories, Ottawa, and used in problems relating to harbor protection, automatic boat steering, and location of lost equipment.

Experience in this field indicated that an airborne type would have immense value in geophysical prospecting; consequently, immediately after the war, work was started to investigate the best way to use it for that purpose. The most advanced airborne type was that developed by the U.S. Naval Ordnance Laboratory. Though early experiments were carried out here with magnetometers designed in the National Research Laboratories, it was soon apparent that the applications of these instruments to geophysical prospecting would proceed most expeditiously by obtaining instruments already well developed. Accordingly, visits were made to Washington that resulted in the assistance and co-operation available there in putting this wartime development into practical use. Magnetic detectors were made available to the National

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Research Laboratories of Canada for government supported research that would further basic knowledge of geophysical and terrestrial magnetic problems.

The instruments used in the experiment described here were those developed by the Bell Telephone Laboratories under contract with the U.S. Naval Ordnance Laboratory and manufactured by the Western Electric Company for the Navy Bureau of Aeronautics. These instruments were obtained through the kind co-operation of U.S. Naval Ordnance Laboratory with whom friendly liaison had been maintained in various other magnetic problems during the recent war. It is our desire here to express thanks to the U.S. Navy, particularly the Bureau of Aeronautics and the Ordnance Laboratory, for making the Magnetic Airborne Detector (M.A.D.) equipment available to us. Thanks are also due the United States Geological Survey for their kindness in sending the M.A.D. equipped plane to Canada to demonstrate this new method of survey and for their help in introducing us to survey methods and map-making technique. Personal thanks are due Dr. L. H. Rumbaugh of the U.S. Naval Ordnance Laboratories, Commander J. W. Joyce of the U.S. Naval Bureau of Aeronautics, Mr. Homer Jensen, formerly of the U.S. Naval Ordnance Laboratories, and Mr. James R. Balsley, Jr., and his associates of the United States Geological Survey.

Parallel with the experiments described here the development of M.A.D. as a prospecting instrument was progressing much more rapidly in the United States. At the time of writing, hundreds of thousands of square miles of country have been covered, and more types of instruments are becoming available, so that their use in prospecting is already a commercial proposition.

The Instrument

The purpose of this instrument is to detect anomalies in the earth's magnetic field associated with the presence of oil or minerals. The sensitive part of the instrument consists of three magnetometer elements (of the second harmonic fluxgate type) mutually perpendicular to one another (2). Two of these elements, operating normal to the earth's field, control servo systems which maintain the third element in the earth's total field. The whole detecting mechanism is towed in a bomb-shaped housing sufficiently far from the aircraft to escape the effects of the magnetic field of the aircraft itself. The variations in the output of the element maintained in the direction of the total field are recorded on a simple recording milliammeter.

To follow the description refer to Fig. 8. Two gimbals whose axes of rotation are normal to each other are driven independently by two servo motors. They are maintained within three-quarters of a degree of the direction of null field and can be corrected with a maximum angular velocity of 20° per sec. The inner gimbal carries a Lucite cylinder containing the three separate magnetometer elements at right angles to each other. The middle element is used as a detector. The outside element perpendicular to

the axis of mounting is called the transverse element, while the other, mounted along the axis of rotation, is referred to as the axial coil. When the axial and transverse elements are in zero field the detector element is in total field. Any movement that destroys this orientation causes the axial and transverse elements to produce a signal proportional to the sine of the angular displacement, while the detector element (in total field) produces a change in signal of less magnitude since it varies as the cosine of the displacement from total field. The mechanism, therefore, operating to keep the detector element in total field, is activated by a signal that is large in comparison to the detector increment—the one that is used for measurement.

The detector element consists of a strip or cylinder of permalloy that is excited by a sinusoidal alternating voltage carried by a coil of wire around the strip of permalloy. In a steady magnetic field the current wave in the coil resulting from the sinusoidal exciting voltage becomes unsymmetrical and a prominent second harmonic appears. This harmonic is roughly a linear function of the steady field and hence it can be used for measurement. The second harmonic (2000 cycles) is separated from the exciting voltage (1000 cycles) by feeding it through a band pass filter of high quality, then to the amplifier, which serves to bring it to a usable level.

A 1000 cycle oscillator (V7 and V8, Figs. 5 and 6) set to ± 3 cycles provides exciting current through 1000 cycle filters to each of the three fluxgate elements. It also feeds a doubling circuit (V2) to produce 2000 cycles for the servo motor's power. A second oscillator (V1) provides an output of 2130 cycles (± 5 cycles), which, when mixed in V6 with the 2000 cycles from the doubling circuit, provides 130 cycles for one phase of each of the two phase servo motors. The output from the detector element is applied to an amplifier (V1 and V4, Figs. 5 and 7) through a 2000 cycle filter. Since the sensitivity of the element is $35 \mu\text{v.}$ per gamma at the input to the amplifier there would be a signal of 2.1 v. on the grid of the first tube if the total field was 60,000 gammas. To eliminate the difficulty of handling a large output signal, a large portion of the average earth's field is balanced out by a direct current through the coil of the magnetometer element. In the present equipment all but 1500 gammas is so neutralized. The remaining average signal of 52.5 mv. is amplified in a conventional a-c. amplifier (V1 and V4) and rectified by a diode (V7), thus producing a d-c. potential (across R19).

As the recording instrument's sensitivity may be adjusted as high as 100 gammas for full scale, the amplified signal corresponding to 1500 gammas plus or minus the variations to be observed is still too high to feed directly to the recorder. The signal is therefore further controlled by imposing a d-c. neutralizing voltage (across R18) so that the output is zero for an arbitrary fixed steady field and produces plus and minus variations from this balance. These variations are fed to a d-c. amplifier (V9 and V10) after going through a sensitivity control circuit in the control box. The output (V10) is recorded directly.

The output from the axial fluxgate passes through a 2000 cycle filter to a second amplifier (V2 and V8, Figs. 5 and 7). It is then mixed with 2130 cycles (V10 and V5, Figs. 5 and 6) producing 130 cycles, which is amplified and fed to the second winding of the servo motor, which acts to bring this element into zero field. The output of the transverse fluxgate passes to a third amplifier and similarly to the second winding of the other servo. The 2000 cycle amplified outputs of the axial and transverse elements are also fed to separate rectifiers (V5 and V6, Figs. 5 and 7), yielding a d-c. component proportional to the square of the second harmonic signal voltage. These two d-c. components are then mixed and fed back through the control box and added to the detector output in an appropriate way to compensate for small and rapid misorientations.

The control box has been mentioned above in connection with the adjusting of the sensitivity and balance. Its functions are as follows. It attenuates the input to the d-c. amplifier so that the recorder scales will read 100, 200, 500, 1500, or 5000 gammas full scale. It effects the compensation required for the small and rapid misorientations referred to in the previous paragraph. It provides for the passing of d-c. increments through the detector coil in 50-, 500-, and 5000-gamma steps. This is accomplished by three parallel shunts across a $22\frac{1}{2}$ v. battery of large cell construction. Voltage is stabilized by rapid discharge to bring the battery to its plateau level. The control box load of 0.78 mill is then permanently applied. The battery remains useful for several months. The 50-gamma steps are obtained by the selection of proper fixed points across a voltage divider. The 500- and 5000-gamma steps are obtained by switching d-c. increments through the detector coil in such a manner that the impedance looking into the battery is constant.

The power pack is operated from 28 v. d-c. mains and consists of two dynamotors in parallel, feeding an electronically stabilized output circuit.

Method of Adjustment

Results with this instrument are obtained in the following manner. The instrument is first put in operation in a magnetically quiet location with no neutralizing d.c. in the coil of the detecting element. After the servo motors place the detector coil in total field, direct current is gradually increased in the detector until the total earth's field exceeds the neutralizing field by 1500 gammas, i.e., the instrument is undernulled by 1500 gammas. (This 1500 gammas is an arbitrary figure and was chosen since it is a suitable value for the type of anomalies encountered.) The recorder now reads zero for reasons shown above.

For calibration the instrument is set in operation and a set of Helmholtz coils is placed coaxially with the detector element so that known fields may be added to or subtracted from the earth's total field.

Values indicated on the recorder are therefore departures from average total field, and the term "profile," as used in this report, refers to the graphs of these variations.

The sensitivity of the instrument may be made to correspond to 100 gammas for full scale on the Esterline Angus recorder, or by various steps to 5000 gammas full scale.

The absolute value of the field, of course, is not known or recorded unless a specific procedure is adopted whereby the instrument is calibrated at a base station whose absolute value is known. For magnetic survey work this is not necessary, as only anomalies are measured. The compensating voltage may be maintained quite uniform and the gain of the amplifiers is reasonably stable so that the total field is probably indicated with a consistency of 1% from day to day. Variation over a short time can be read to a few gammas and drifts are very small when temperatures are steady.

Note:—Just before the work at the airport was terminated, the apparatus was operated continuously for a few days in an effort to observe diurnal changes. The detector was placed in a weatherproof box 200 ft. from the hangar while other equipment remained inside. Temperature has a considerable effect on the indicated field reading. However, since compensation is made for such changes in the Survey Procedure no further time has been given to the matter.

Survey Procedure

The area selected for the experimental survey lay some 25 miles west of Ottawa. The survey was conducted by flying half-mile grids at each of three elevations, 5000, 1000, and 500 ft. The method of survey was as follows. Half-mile grid lines (north-south) were drawn on one-mile-to-the-inch topographical maps. (Suitable aerial mosaics were not available.)

The crew of the Anson plane carrying the apparatus consisted of the pilot, navigator, magnetometer operator, and usually a fourth member who operated the winch, etc. The pilot was responsible for following the grid lines and maintaining constant altitude and speed. The navigator traced the plane's course on the topographical map and aided the pilot in his duty of following the grid lines by indicating land marks.

While flying the north-south grid, a note was made of the magnetically flat and the magnetically rough areas. This enabled the selection of an area suitable for flying an east-west base line to bring all north-south lines to a common denominator necessitated by diurnal and other magnetic changes and instrument drift.

A Sonne continuous strip camera (Fig. 3) was in operation during all flights. When passing over easily identifiable points, the navigator operated a foot pedal that linked the magnetic reading with that particular geographical position. This was accomplished by means of a photographic and electro-magnetic system.

The recorder used was an Esterline Angus. While it was satisfactory in other respects, we found the chart rather narrow for the purpose. During flight, it is therefore necessary to observe the meter and maintain proper

placement of the pen by applying and recording known increments to the neutralizing circuit. This results in a discontinuous profile on the recorder tape. The control box and linkages from it to the recorder (Fig. 4) so operate that increments in the neutralizing field and changes in sensitivity are printed on the tape.

By reference to the developed film, the flight lines are redrawn to coincide with the actual path of the plane. The geographical check numbers are also plotted on these flight lines from the film. The Esterline Angus tape with the magnetic record is then placed on the graph rectifier (Fig. 9). This is a machine with a system of levers and two movable tables to (a) convert the curvilinear record of the recorder tape to one with rectilinear co-ordinates, (b) expand or compress the horizontal scale so as to fit the desired map scale, (c) increase or decrease the vertical scale, and (d) fit the offset segments of the magnetic profile on the Esterline Angus tape into a continuous profile. The east-west base line profile values are then established where they geographically coincide with the north-south flight line profile values, and the comparison is noted. If there has been no terrestrial magnetic change, if there has been no instrumental drift, and if the geographical positioning is exact—then these values will be equal. If they are unequal it is necessary to adjust the reference line for each north-south profile to compensate for this difference. Flight lines flown over a period of hours, days, or months can therefore be tied together by a base line that can be flown in a few minutes, thus eliminating the possible errors due to drift, temperature, etc.

Suitable magnetic intensity values are next read from the north-south profiles (Fig. 10) and transferred to the flight lines (Fig. 11) obtained from the continuous strip film. The magnetic highs and lows are noted and magnetic contours drawn.

Three factors must be taken into account before magnetic values can be assigned a geographical position. They are distance of bird behind camera, lag due to recording, and perpendicularity of the camera.* Probably the simplest method for compensating for all three factors is to fly the base line first in an east-west direction then in a west-east direction. Peaks on these profiles should coincide when tied to geographical positions. If they do not coincide, a correction must be applied to all profiles, with due respect to direction of flight, and will be equal to half the distance between the baseline peaks.

Conclusions

The final contours are shown in Figs. 12, 13, and 14. All three levels were flown on half-mile grids. In the working up of the results this grid seemed quite suitable for the 5000 ft. level but was quite inadequate for the 500 ft. level.

The area was flown with the use of one-inch-to-the-mile topographical maps, which proved wholly unsuitable for wooded areas. In sparsely settled regions

* The Sonne camera is gyro controlled for roll but has no compensation for pitch.

good aerial mosaics are essential if precision results are desired. The completed maps can be no more accurate than the positioning methods. It would be desirable if the present strip camera were stabilized for pitch as well as for roll, especially in rugged areas where the plane must climb rapidly on occasions.

A recording radio altimeter AN/APN1 was used, but it was not considered useful to attempt any correlation from the records when the 5000, 1000, and 500 ft. readings were already plotted. If something better than just general reconnaissance is required in magnetic mapping then an altimeter of much greater accuracy would be an improvement. In fact if sufficient precision were acquired it would be possible to construct topographical maps as well.

While the "winch, cable, and bird" has proved very satisfactory it adds to the need for greater precautionary measures. In this respect it is strongly recommended that (a) the amount of tow cable released from the winch be varied—say a foot or so per month of flying—so that the flexing occasioned at the point of suspension will not cause fatigue breakage (this flexing at the bird itself is taken up by a universal joint); (b) the whole apparatus be checked periodically; (c) a permanent, positive, semiautomatic device be installed for cable release in case of emergency; and (d) the whole system be subjected to periodic 500 lb. static load tests.

At the time of writing, the apparatus has been transferred to an inboard installation in a Canso aircraft. This eliminates the hazards associated with the towed bird system, which is used when only small planes are available.

This new method of prospecting places a powerful tool in the hands of the mining industry. The slow, laborious, and expensive method of point to point measurement can now be replaced by a cheaper one yielding a continuous magnetic profile at the rate of 120 m.p.h. Small surface anomalies that might otherwise mask or distort ground measurements are lessened, or completely wiped out, leaving only the general picture from which the over-all geological interpretation can be made. Drift and diurnal variations are minimized by the speed of operation and by the method of magnetic baseline corrections. There can be no doubt that the era of the dip needle for purposes of reconnaissance has disappeared, and will in future be reserved for necessary detailed surface work. The way is open for complete magnetic world coverage, which in time will aid in the better utilization of natural resources.

A modified instrument of this type will have extreme value in solving future navigational problems. Other instruments will be designed with a sensitivity as high as 0.1 gamma. Further, the principle will be applied in the construction of instruments for medical purposes, law enforcement, the location of lost objects, and laboratory and commercial use. The design of an absolute instrument for the recording and measurement of the earth's terrestrial field is in progress in this laboratory.

Acknowledgments

It is desired to express appreciation to Dr. R. W. Boyle for his continued aid and guidance, and to Dr. D. C. Rose for his constructive criticism.

Credit is due Mr. George Shaw, Geologist, Department of Mines and Resources, for his interest in this project since its beginning in 1946. To Mr. G. S. Levy of the Flight Research Section at Arnprior, we express our thanks for his co-operation in providing the necessary aerial facilities.

Fig. 1 appears through the courtesy of Mr. A. G. Roberts of the Capital Press Service in Ottawa.

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FIG. 1. *M.A.D. in flight.*

PLATE II



FIG. 2. *M.A.D. installation—Anson.*

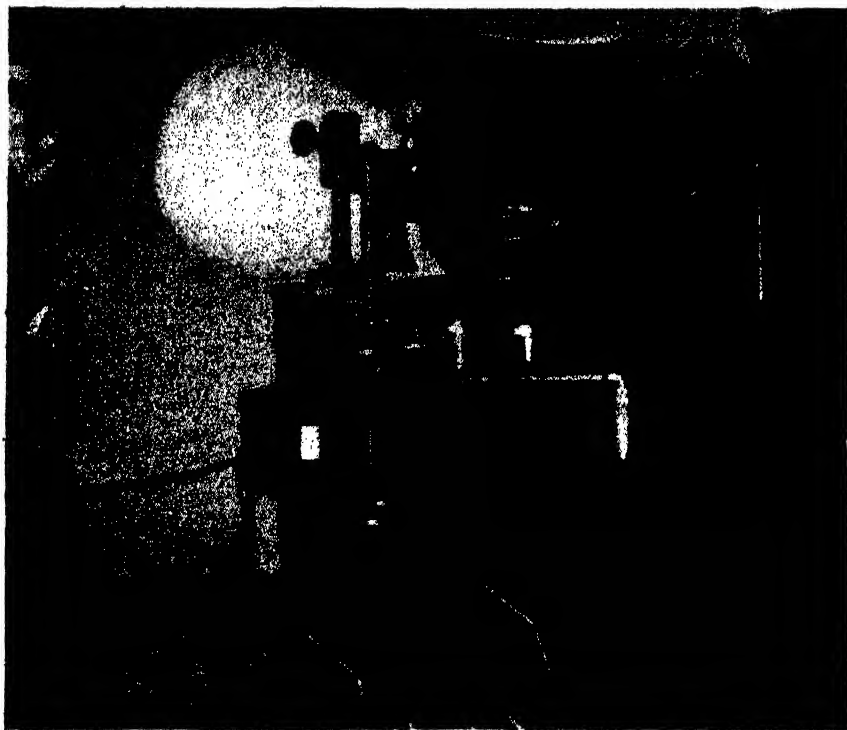


FIG. 3. *M.A.D. installation—Anson.*

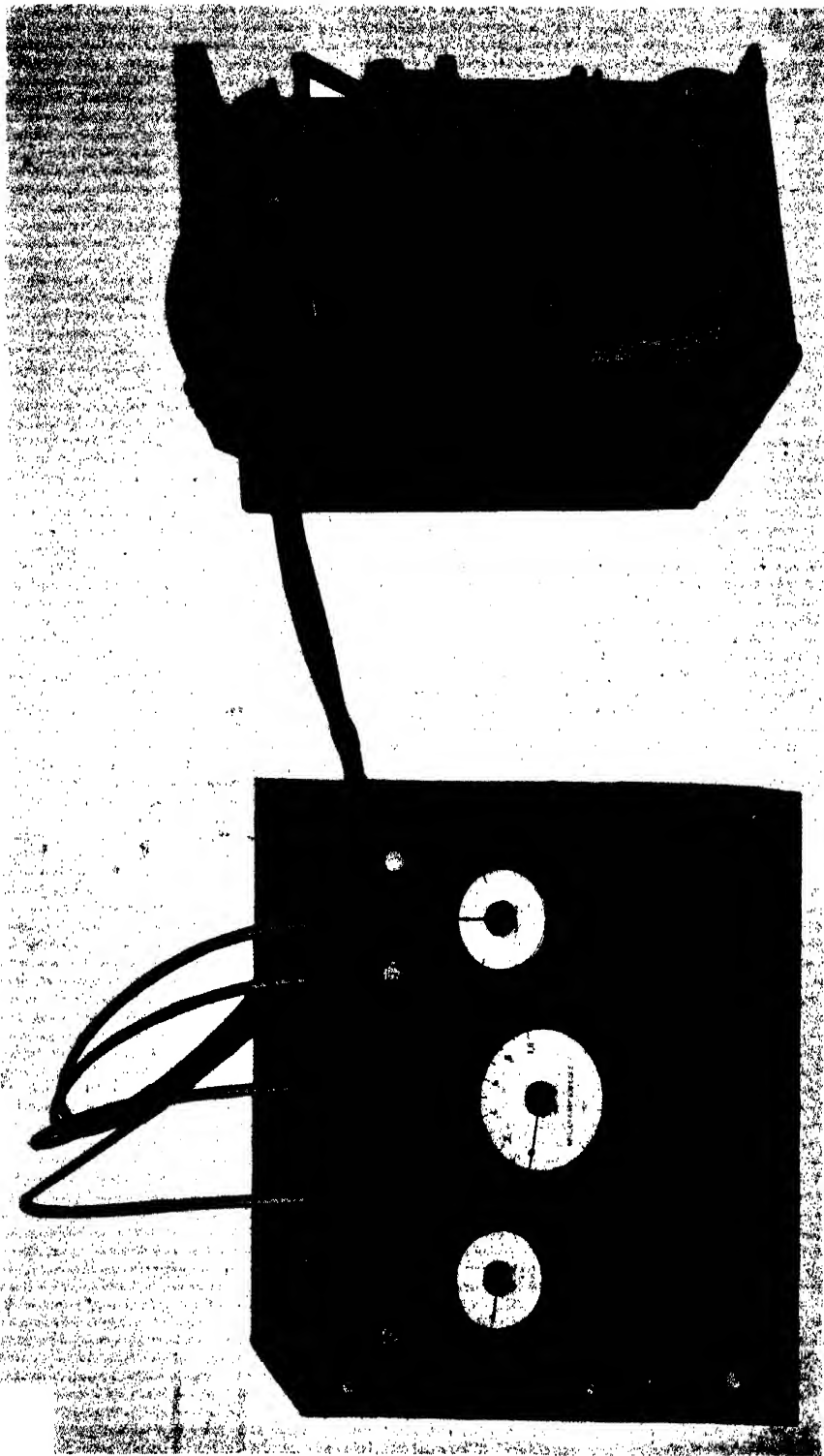


FIG. 4. Control box and recorder.

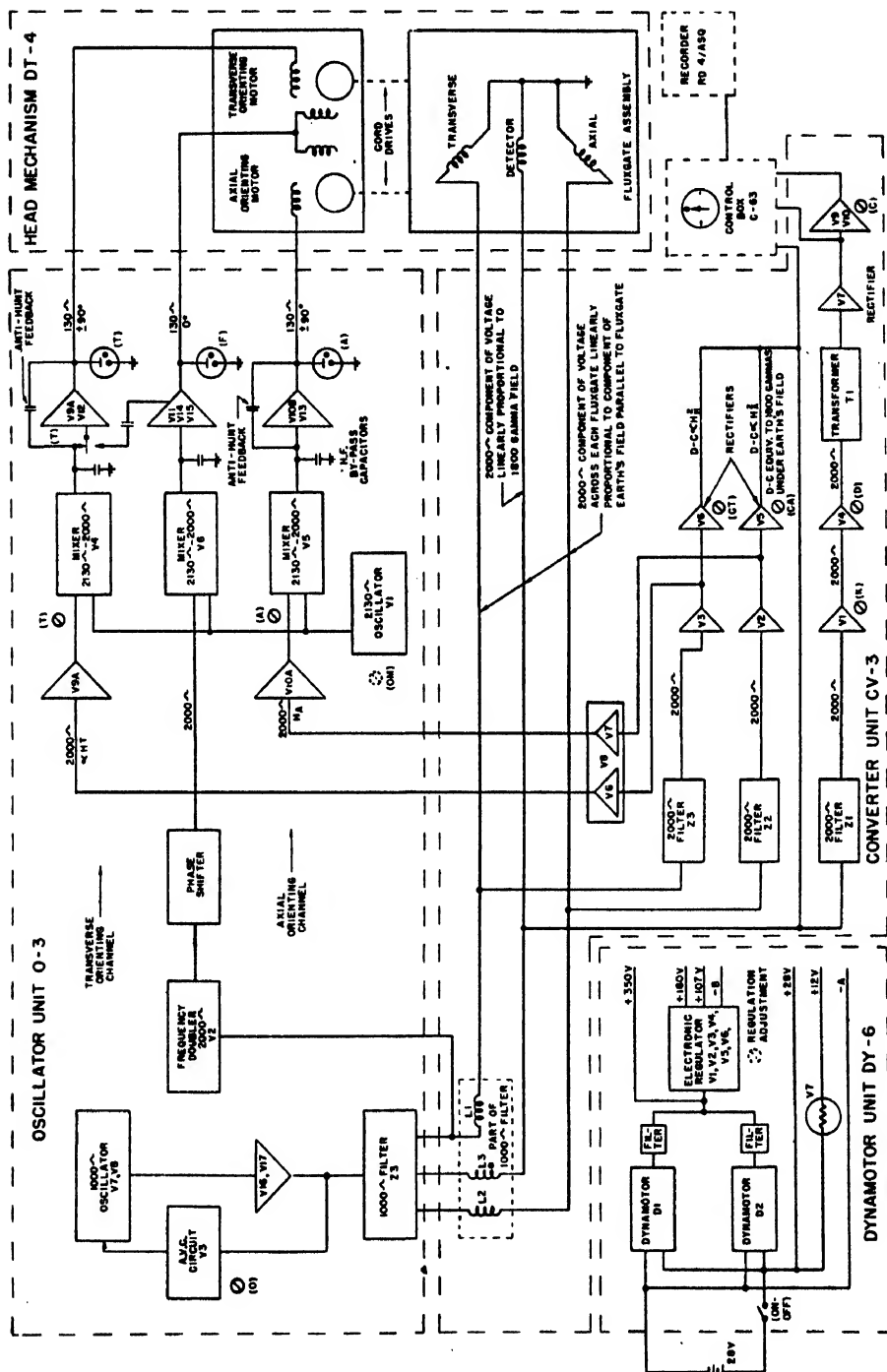


FIG. 5. Block diagram. In this diagram, for "1800" read "1500".

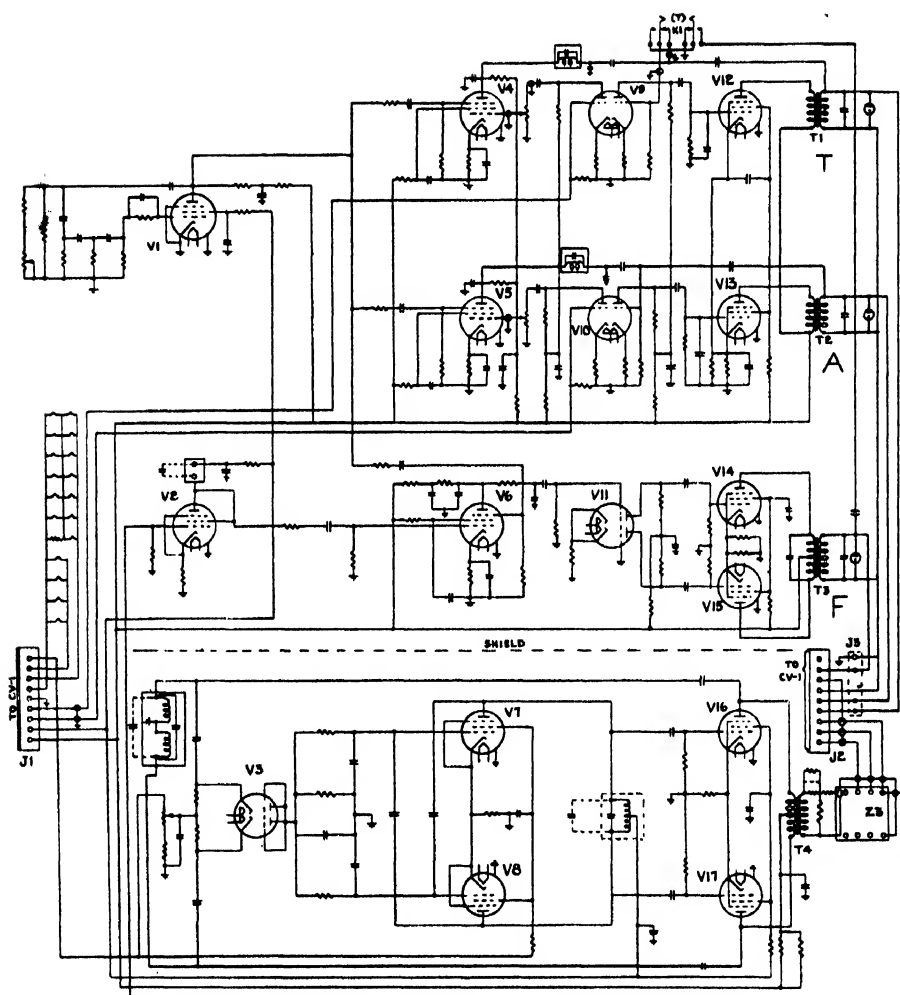


FIG. 6. Oscillator.

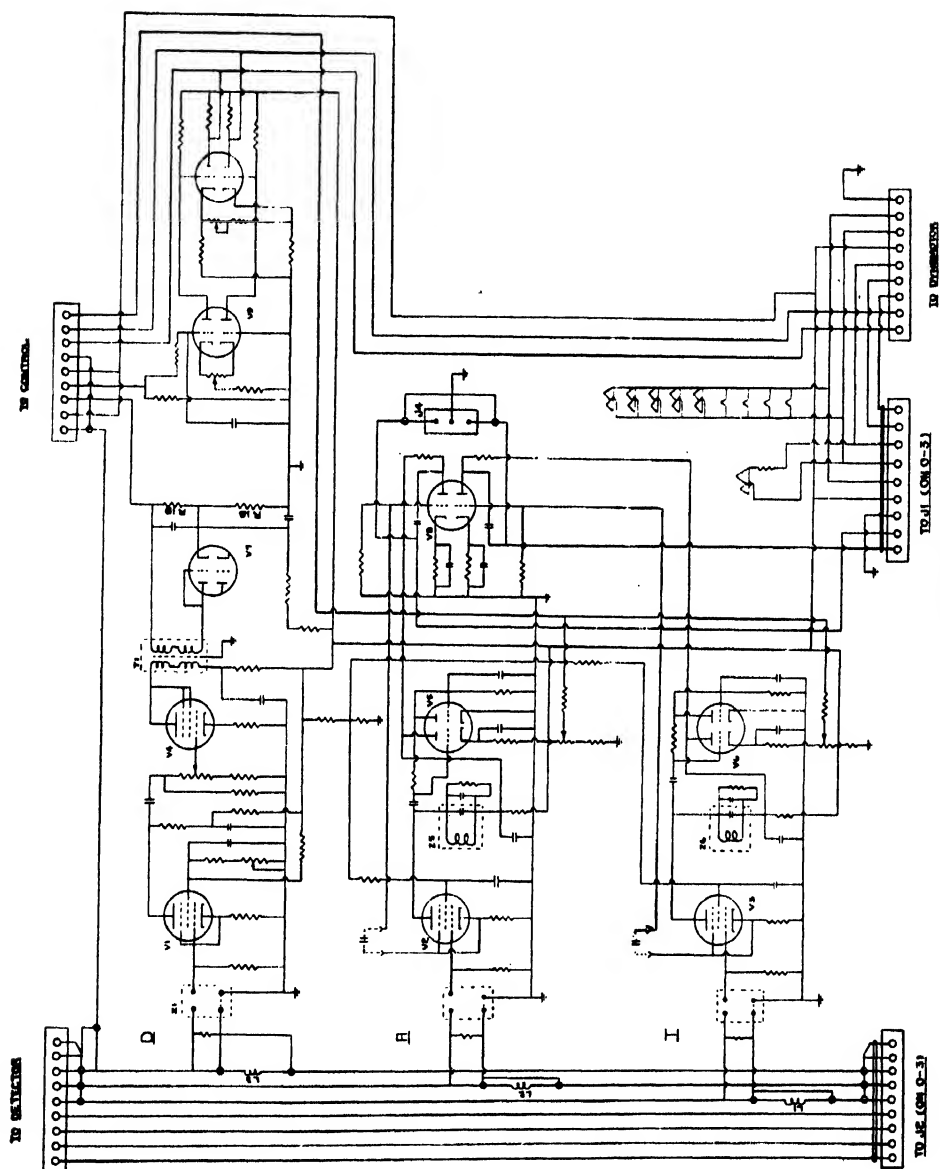


FIG. 7. Converter unit.

FIG. 8. Magnetometer head, showing orienting gimbals and slip ring contacts. The three separate magnetometer elements are housed in the central Lucite cylinder.



FIG. 8.

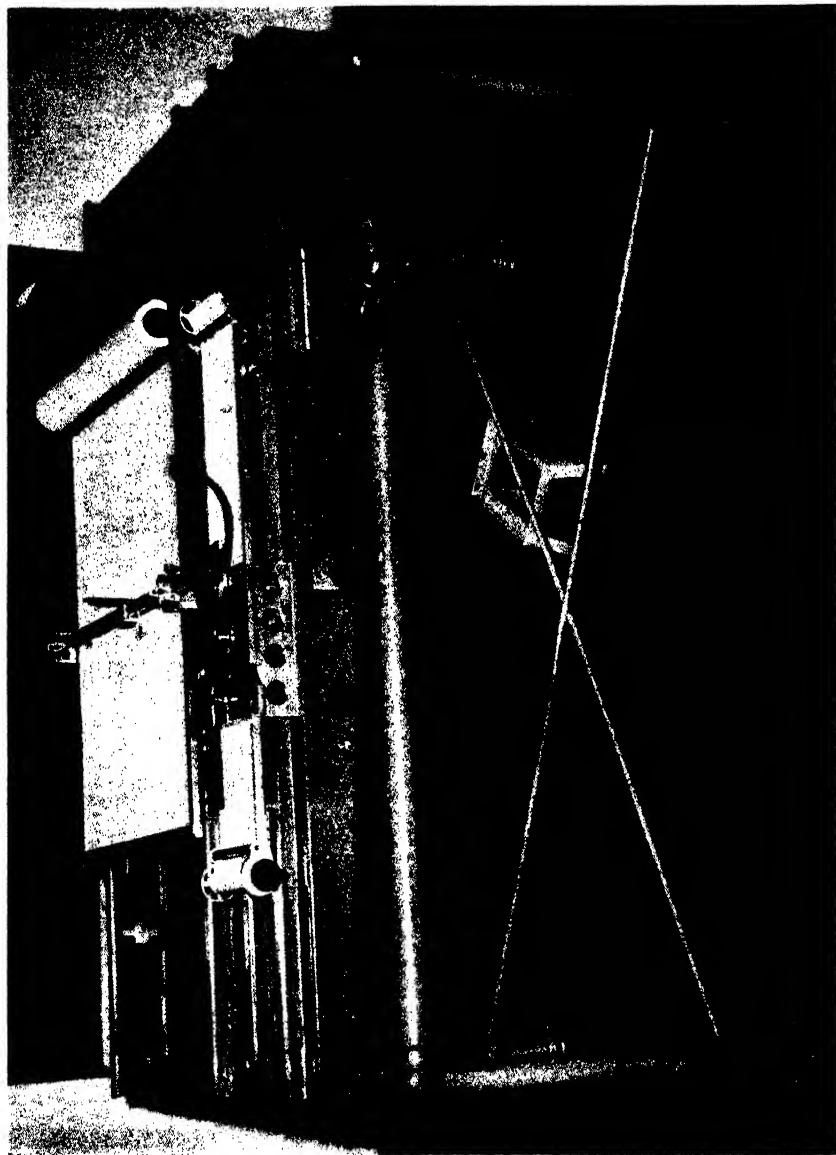


FIG. 9. Graph rectifier.

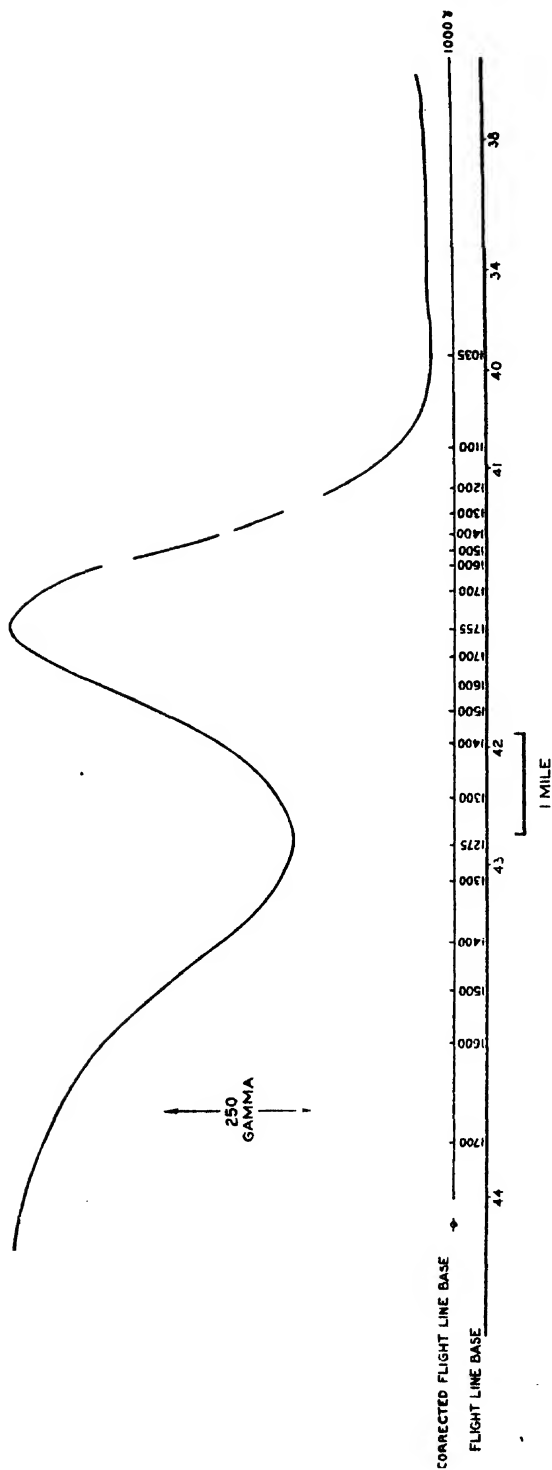


FIG. 10. Magnetic profile. Line 17, 5000 ft. level, 500 γ sensitivity.

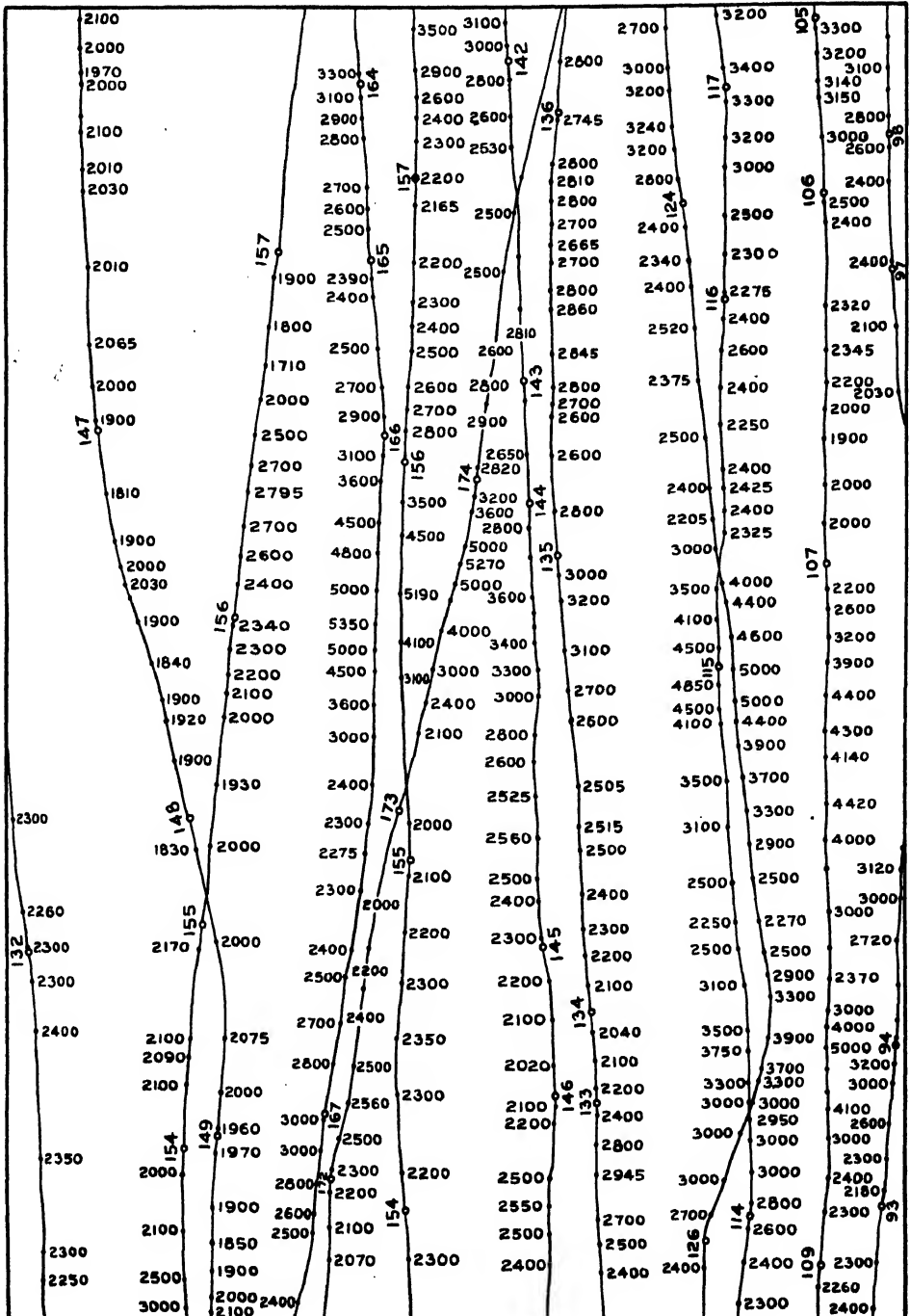


FIG. 11. Flight lines with profile values (1000 ft. level).

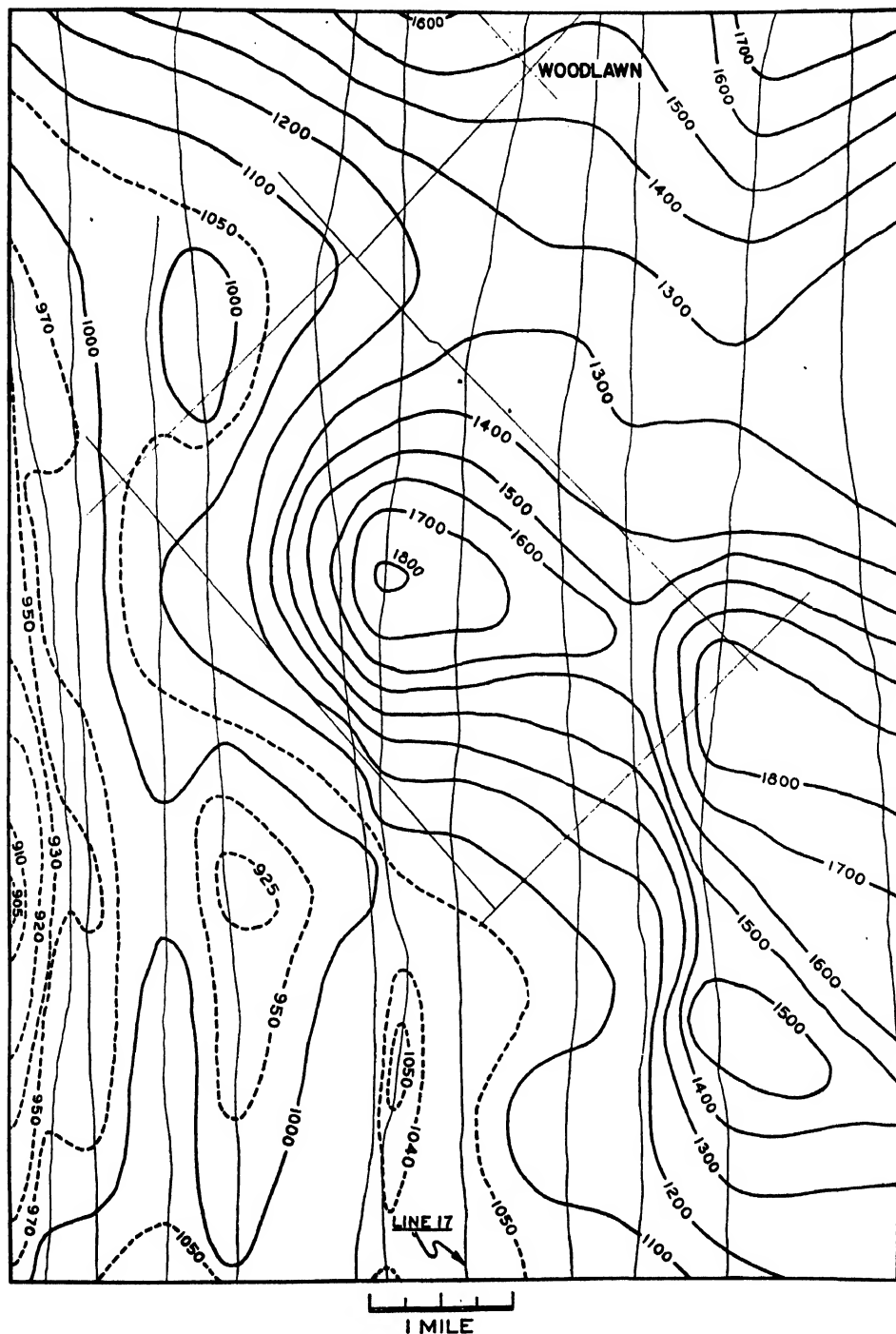


FIG. 12. M.A.D. test survey. Carp area. 5000 ft. level.

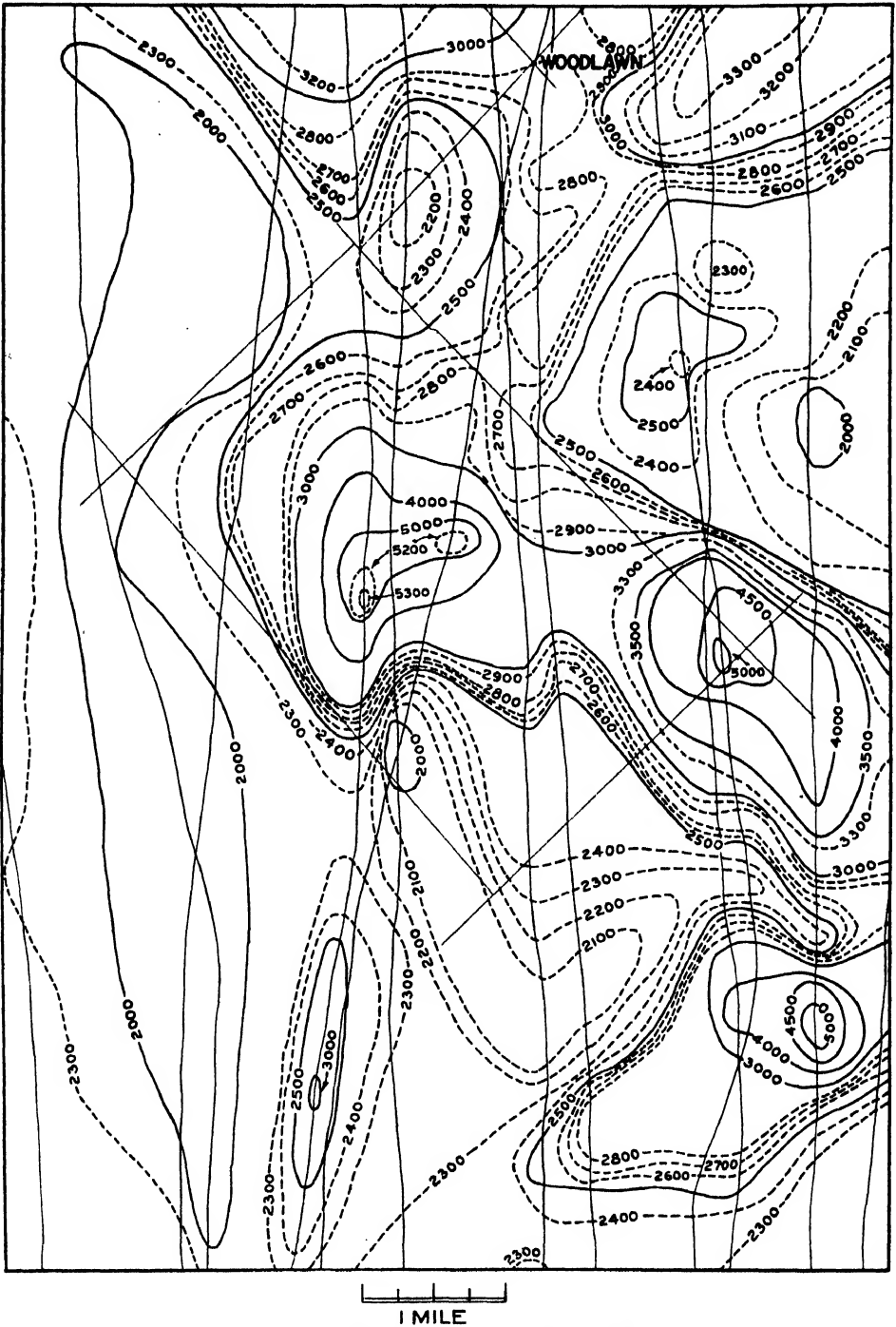


FIG. 13. *M.A.D. test survey. Carp area. 1000 ft. level.*

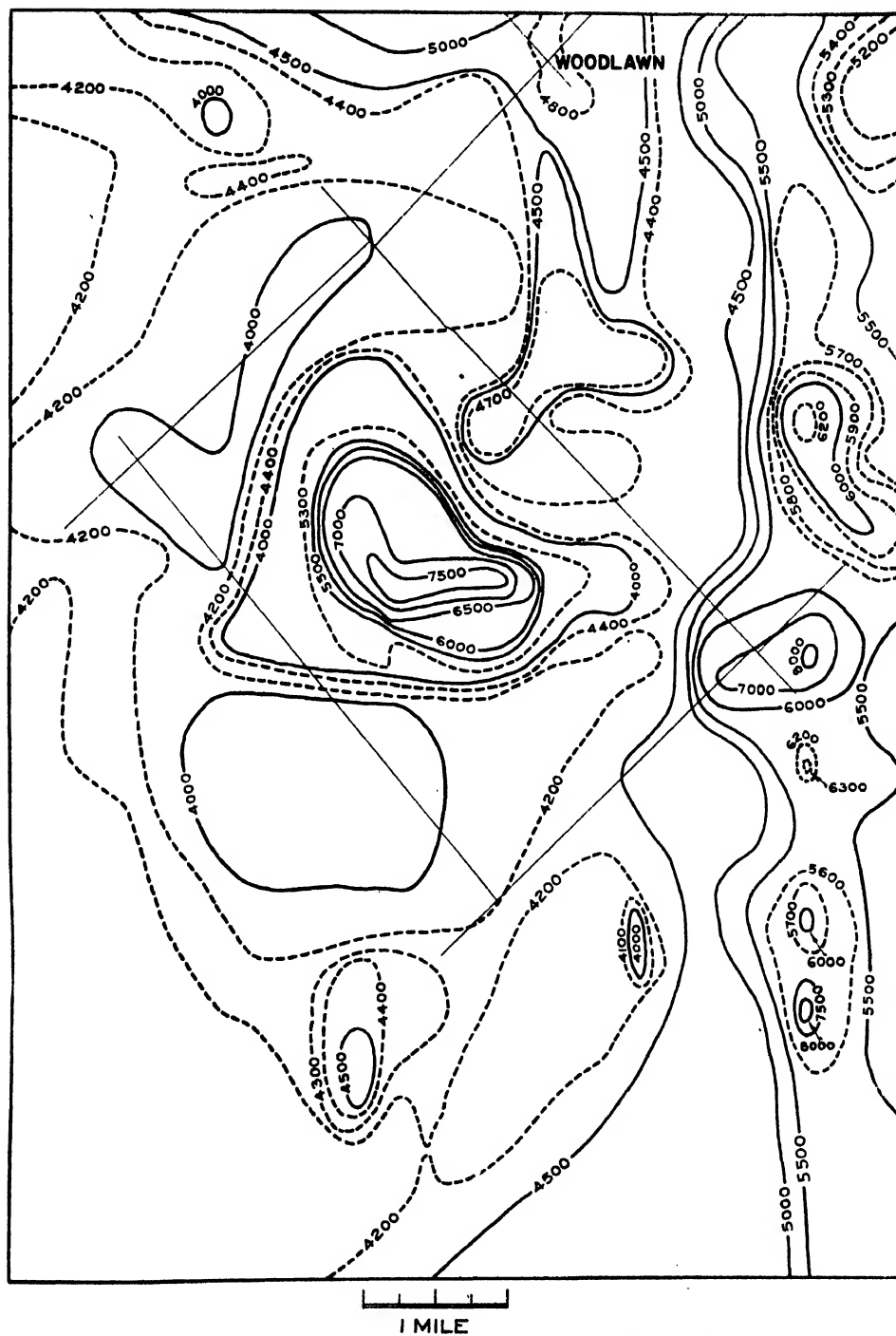


FIG. 14. M.A.D. test survey. Carp area. 500 ft. level.

THE FUNDAMENTAL ACTION OF INTENSIFYING SCREENS IN GAMMA RADIOGRAPHY¹

E. L. HARRINGTON², H. E. JOHNS³, A. P. WILES⁴, AND C. GARRETT⁴

Abstract

The nature of the intensifying action of lead screens and Patterson screens has been investigated for gamma radiography. For the lead screens used it was found that nearly 52% of the blackening of the film is due to electrons ejected from the front screen and nearly 48% due to electrons ejected from the back screen. The blackening of the film due to the absorption by the film itself of the radiation is small. Similar results were obtained with Patterson screens except that about 10% of the effect of the screens is due to low energy radiation (light) which was stopped by 3 mgm. per cm.² of aluminum.

Introduction

It is standard practice in gamma radiography to place the film between sheets of lead when making an exposure. The sheet of lead in front of the film usually has a thickness between 0.003 in. and 0.005 in., while the back screen may vary from 0.020 in. to 0.040 in. in thickness. With these screens in place, the exposure required for a photograph of a given casting is very much less than is required when the lead sheets are not used. For this reason the lead sheets are referred to as intensifying screens.

The cause of the intensification obtained with these screens was investigated by totally removing the effect of each screen in turn, and finally the effects of both of them, in order to find that of the film alone. The effect of the front screen was eliminated by separating the screen from the film and then applying a magnetic field in the region between the screen and the film strong enough to prevent any electrons ejected from the screen from reaching the film. For the back screen effect, an evacuated space was provided, instead of a back screen, sufficiently long to assure a negligible effect due to backward-moving electrons and radiation from the walls of the container. Finally, by a combination of both methods, the direct effect of the radiation on the film itself was determined.

Experimental Arrangement

The source of gamma rays used was a capsule containing 203.5 mgm. of radium, which was placed in a brass container having walls $\frac{1}{8}$ in. thick. To keep scattering to a minimum, a lead diaphragm, giving a total conical angle of 7° was used, and all interior surfaces of the apparatus were lined with light cardboard to stop scattered electrons without appreciable production of

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X-rays. The source-to-film distance was kept constant at 9 in., and all exposures were made through $\frac{1}{2}$ in. of brass rather than steel since the apparatus had to be of nonmagnetic material. The radiographic properties of brass are close enough to those of steel to make the results applicable to either. The front lead screen was 0.003 in. thick, and the back screen 0.020 in. For the Patterson screens the industrial combination No. 245, with the thin screen in front, was used. Kodak No-Screen film was used throughout and developed in Kodak X-Ray Developer, at 20° C., for five minutes, with agitation at the end of every minute. The film densities were read on a Marshall Transmission Densitometer.

To provide a constant check on the work, a control exposure was made and developed with each set of exposures. For this, a cardboard film holder, having a set of lead screens, or Patterson screens, the same as those used in the other parts of the experiment, was placed under a $\frac{1}{2}$ in. brass plate and given a constant exposure with a source to film distance of 9 in. The constant densities obtained for the control experiments indicated consistency of exposure, development, and film characteristics. As well as this, an unexposed strip of film was developed with each set of exposures to give the background density. The latter remained constant at 0.32.

Fig. 1 shows the exposure factor ($\frac{\text{mgm.} \times \text{min.}}{\text{in.}^2}$) versus film density for the lead screens (Curve A), and the Patterson screens (Curve B) with Kodak No-Screen Film. These exposures were made with the film in firm contact with both the front and the back screen, the front screen being fastened to a

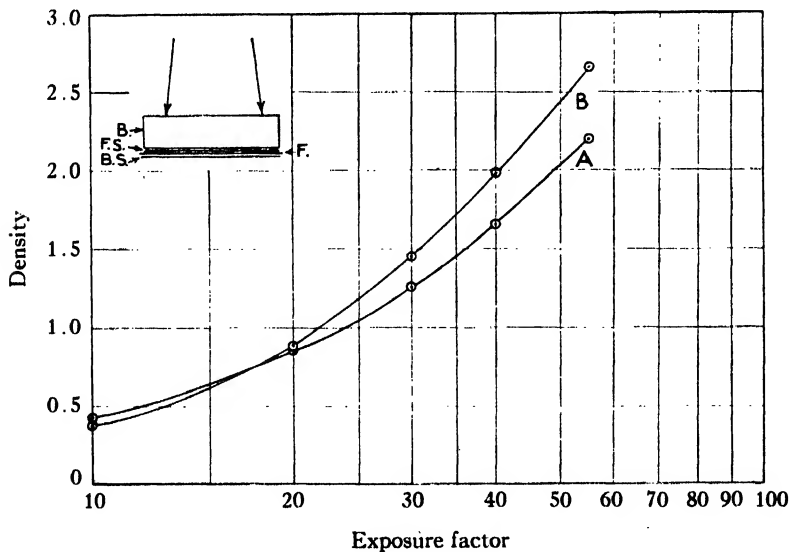


FIG. 1. Density versus exposure factor for "No-Screen" film. Curve A was taken using a lead front screen 0.003 in. thick and a lead back screen 0.020 in. thick. Curve B was taken using Patterson Industrial Combination No. 245. The film was exposed through $\frac{1}{2}$ in. of brass. (B—brass, F.S.—front screen, F—film, B.S.—back screen.)

brass plate $\frac{1}{2}$ in. in thickness. In the following experiments, an exposure factor of 55 was used with the lead screens, and 45 with the Patterson screens. These exposure factors give a density of 2.21 in each case (see Fig. 1.)

Part I

Lead Screens

(a) *The Effect of the Front Screen*

Consider a magnetic field applied parallel to the front screen and perpendicular to the incident beam of gamma rays, as in Fig. 2. All ejected electrons will move in circular paths in the magnetic field, the curvatures of the paths

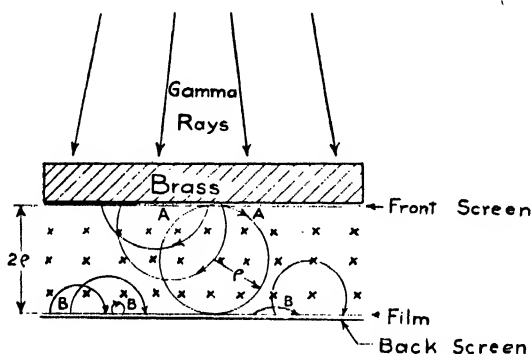


FIG. 2. The schematic arrangement of the apparatus used for determining the effect of the front screen.

being dependent on the energy of the electrons and on the strength of the magnetic field, and their excursions from the front screen on the direction of ejection from the screen into the field. Those that are ejected tangentially to the front screen towards the right (path A, Fig. 2) will be the hardest to prevent from reaching the film. Electrons that follow a path having a radius of curvature greater than ρ and that are ejected tangentially (path A) will strike the film. 2ρ is the distance between the film and the screen and had the value 2.35 cm. in the apparatus used. It follows then that electrons with energies corresponding to values less than $B\rho$ (where B is the flux density) would all be prevented from reaching the film regardless of their directions of emission. Some electrons (see B, Fig. 2) will be ejected in a backward direction from the film itself, and these will be curved back into the film by the magnetic field and produce some darkening.

Fig. 3 shows the experimental arrangement used to determine the effect of the front screen. N and S are the poles of an electromagnet capable of giving a field of 5400 gauss across a gap of 3 cm. The film holder consisted of an air-tight metal box, which could be evacuated to cut down the scattering from the air in the box. The front screen was fastened to the $\frac{1}{2}$ in. brass top

of the box, while the film and back screen were supported by a series of spacers. These spacers made it possible to vary the separation d between the front screen and the film from 1.50 cm. to 6.50 cm. in a series of five steps.

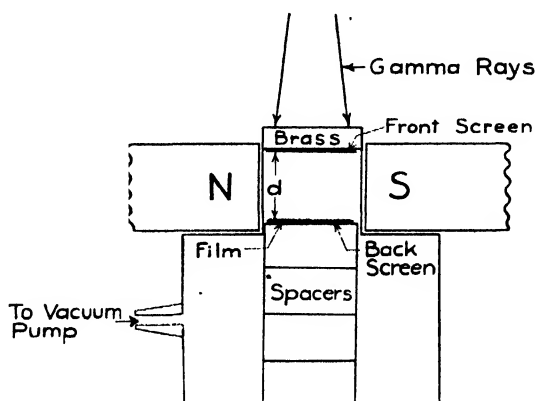


FIG. 3. Diagram of the apparatus used to determine the effect of the front screen.

Some of the exposures made to determine the effect of the front lead screen are listed in Table I. Only the average values of the densities obtained are

TABLE I

SUMMARY OF RESULTS OF THE DETERMINATION OF THE EFFECT OF THE LEAD FRONT SCREEN

Separation between front screen and the film, d cm.	Magnetic field, gauss	$B\rho$, gauss-cm.	Average density
0.00	0	0	2.21
2.35	0	0	1.21
2.35	1500	1760	1.05
2.35	2790	3280	0.93
2.35	4240	4980	0.89
2.35	5385	6325	0.89

given. The individual measurements agreed to within about 5%. These results appear graphically in Fig. 4.

It is seen from Table I that for zero magnetic field, a change in the distance between the front screen and the film from 0 cm. to 2.35 cm. causes a decrease in density from 2.21 to 1.21. A considerable decrease is to be expected as the distance d is increased. Also it will be seen from Fig. 4 that the density is constant for $B\rho$ equal to or greater than 4980 gauss-cm.

To correct the density at maximum magnetic field to zero centimeters of separation, a series of exposures was made with separations between the front screen and the film of 1.50, 2.35, 3.70, 5.00, and 6.50 cm. using the apparatus shown in Fig. 3. For all these exposures, the maximum field of 5385 gauss was

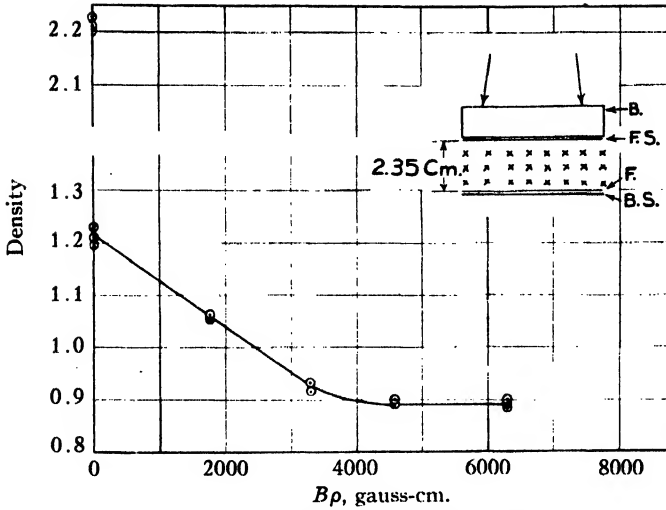


FIG. 4. Graph showing the variation of film density with magnetic field when the electrons ejected from the front lead screen are curved back by the application of the magnetic field shown.

applied in the region between the front screen and the film. The result of this series of exposures is shown in Fig. 5, in which density is plotted against

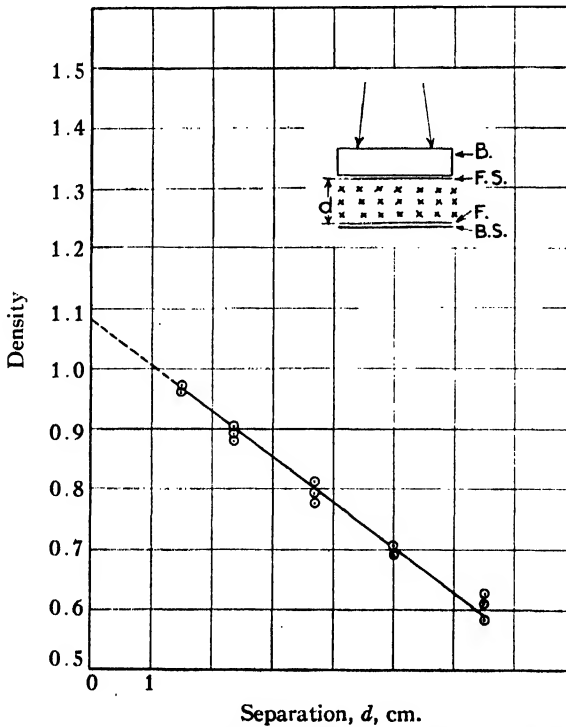


FIG. 5. Graph showing the variation of the film density with the separation d between the front lead screen and the film when all the electrons ejected from the front lead screen are prevented from reaching the film by the magnetic field.

the separation between the front screen and the film. For all the points plotted the magnetic field of 5385 gauss was sufficient to ensure the return to it of all the electrons emitted by the front screen in the forward direction. That is, these points correspond to points beyond the bend in the curve shown in Fig. 4. From Fig. 5, it is seen by extrapolation that for zero separation the density would be 1.08. This means that removing the effect of the front screen decreases the density from 2.21 to 1.08, a reduction of 51.2%.

From that portion of the curve in Fig. 4 where the density is constant it is possible to determine the maximum energy of the electrons emitted from the front screen owing to the action of the incident gamma rays. The value of $B\rho$ where the density becomes constant is 4980 gauss-cm., which corresponds to an electron energy of 1.07 Mev. for an electron ejected tangentially or 2.5 Mev. for an electron projected normally. The maximum energy of the incident gamma ray from radium is 2.2 Mev., which can eject from lead a photoelectron of energy 2.1 Mev. The probability of the photoelectron's being ejected in the forward direction is considerably greater than at an angle of 90° . When one considers that the 2.2 Mev. component of the gamma rays from radium is very small, we see why the bend of the curve in Fig. 4 appears in the region indicated.

(b) *The Effect of the Back Screen*

It was impossible to use a magnetic method to determine the back screen effect owing to the fact that there are a great many more electrons ejected from the film in the forward direction than in the backward direction. These would be curved back into the film by the magnetic field, and cause a very great increase in the density of the film. In a trial experiment the density obtained with 0 field was 1.42 and when the maximum field of 5385 gauss was applied the density rose to 1.62. For this reason, it was decided to remove the effect of the back screen by the use of distance only. The apparatus represented in Fig. 6 was used. It included a bell jar, 7 in. in diameter and 16 in. high; sealed onto a $\frac{1}{2}$ in. brass plate. The front screen was fastened to the brass plate and the film held in firm contact with it. The bell jar was evacuated for all exposures, with all other conditions the same as for the front screen determination.

Exposures were made also with the back screen in contact with the film to serve as a check, and densities of 2.21 were obtained. This value is in agreement with Table I and Fig. 1 for an exposure factor of 55. Then the back screen was removed entirely, leaving only the film and the front screen, and several additional exposures were made. These gave densities that averaged 1.13. This means that the removal of the back screen reduced the density from 2.21 to 1.13, a reduction of 49.0%.

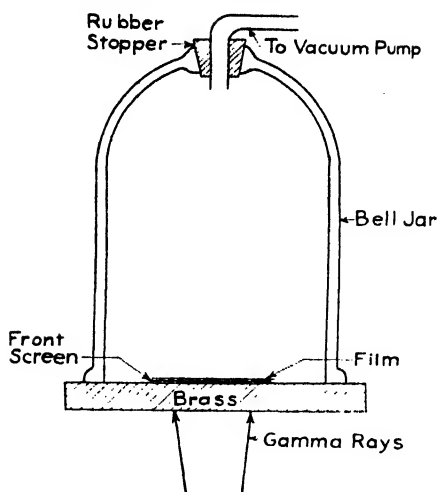


FIG. 6. Diagram of the apparatus used to determine the effect of the back screen.

(c) *The Effect of the Film Alone*

To determine the effect of the film alone, a combination of the two methods was employed. Fig. 7 shows the apparatus employed; it made use of an

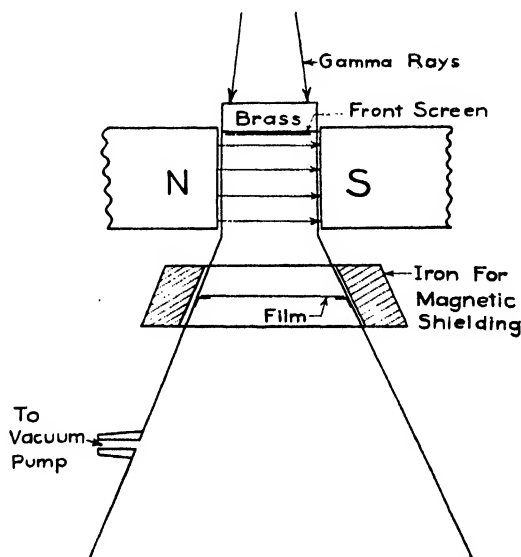


FIG. 7. Diagram of the apparatus used for the determination of the effect of the film alone.

air-tight box $13\frac{1}{4}$ in. high having a brass top $\frac{1}{2}$ in. thick to which the front screen was attached. The film was supported $3\frac{3}{4}$ in. below the front screen, and a magnetic field of 5385 gauss was applied in the region indicated. A heavy iron bar was placed around the box in the region of the film to act as a magnetic shield and thus to provide a region of zero field at the position of

the film. This is necessary to prevent electrons ejected from the film from curving back into it and thus causing an increase in density. The bottom of the box was 9 in. below the film, and no back screen was used. The box was evacuated for all exposures.

Several exposures were made with the same conditions as in the other parts of the experiment described above. These gave an average density of 0.08 when, as in all cases, the background of 0.32 was subtracted. When the effects of both the front and back screen are removed, the density falls from 2.21 to 0.08; this indicates that the percentage effect of the film alone is 3.6%.

Part II

Patterson X-Ray Intensifying Screens, Industrial Combination No. 245

(a) Front Screen

The effect of the front screen was determined in the same manner as for the lead front screen but with the addition of one further step. This consisted of taking an additional series of exposures, varying the magnetic field as before, but having the front screen covered with a thin sheet of aluminum foil (3.05 mgm. per cm.²). This thickness of foil would not absorb any appreciable number of the electrons from the front screen yet would absorb the light emitted by these screens when they are irradiated with gamma rays. Fig. 8 shows the results of both these series of exposures, Curve A with the front screen alone, and Curve B with the front screen covered with aluminum foil.

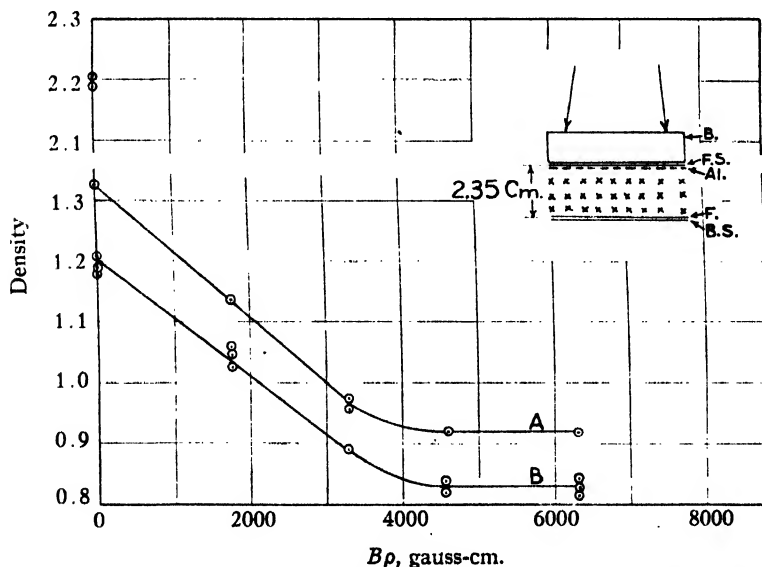


FIG. 8. Graph showing the variation of film density with magnetic field when the electrons ejected from the front Patterson screen are curved back by the application of the magnetic field shown. For Graph B the Patterson front screen was covered by aluminum foil 3.05 mgm. per cm.² thick. For Curve A no aluminum was used.

Fig. 9 shows the result of varying the spacing between the front screen and film, and is analogous to Fig. 5 for the lead screens. From this graph it is seen that a density of 1.05 would be obtained at 0 cm. separation if all the

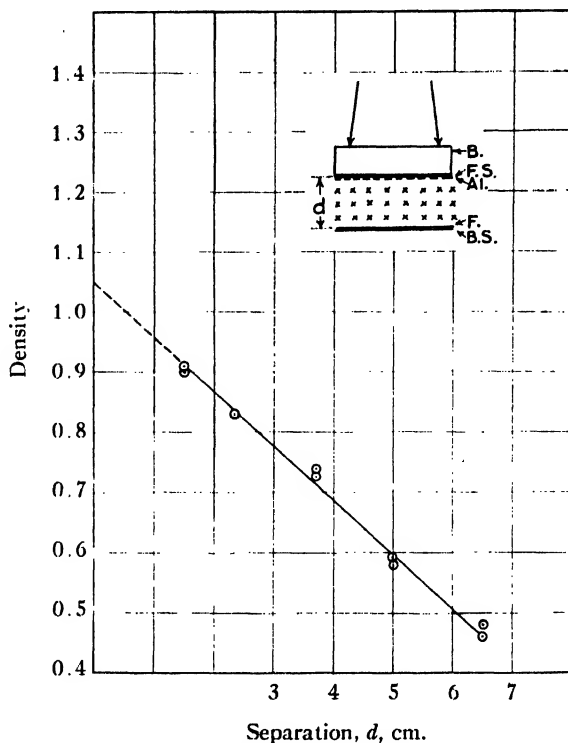


FIG. 9. Graph showing the variation of the film density with the separation d between the front Patterson screen and the film when all the electrons ejected from the front screen are prevented from reaching the film by the magnetic field, and radiation from the front screen is filled by 3.05 mgm. per cm^2 of aluminum.

electrons from the front screen were prevented from reaching the film and if radiation from the front screen that can be absorbed by 3.05 mgm. per cm^2 of aluminum were stopped. This corresponds to a reduction in density of 1.15 and gives a Patterson front screen effect of 52.3%. From the displacement of the two curves in Fig. 8, it is seen that the light energy that can be stopped by 3.05 mgm. per cm^2 of aluminum makes up 9.8% of the total effect of the Patterson front screen.

(b) Patterson Back Screen

The effect of the Patterson back screen was determined in exactly the same way as for the lead back screen. Exposures with both front and back screens present gave a density of 2.20, and, when the back screen was removed and a vacuum chamber employed, the density fell to 1.15. This means a reduction in density of 1.05, and gives a Patterson back screen effect of 47.8%.

(c) *The Film Alone*

The effect of the film alone was determined also for the Patterson screens in order to obtain a check on the work. The determination was made in exactly the same manner as when using the lead screens except in this case the front screen was covered with aluminum foil. The density obtained using an exposure factor of 45 was 0.075; this gave an effect of 3.4% for the film alone.

To determine whether bombardment of the lead screen by gamma radiation produces any appreciable amount of radiation in the visible or in the ultra-violet regions, two further exposures were made with the lead screens. The first one was made with a separation of 2.35 cm. between the front screen and the film with a field of 5385 gauss and the second similarly but with 3.05 mgm. per cm.² of aluminum in contact with the lead front screen. These two exposures gave the same density; this indicated that if any radiation was produced in the lead front screen, it was penetrating enough to pass through 3.05 mgm. per cm.² of aluminum.

Discussion of Errors

The gross percentage error for the experimental work was about 4%, which is made up of several factors. The source-to-film distance could be reproduced to $\pm 1/16$ in., and the exposure times (21.9 min. for the lead screens, 18 min. for the Patterson screens) could be reproduced to ± 3 sec.

The processing of the exposed film was under very close control, as shown by the fact that the density of the control exposure and the unexposed background strip never varied more than ± 0.02 .

Scattered radiation would increase the film density in all cases over that due to any direct radiation and to the electrons themselves. However, with the 7° collimator used in all parts of the experiment, and with all inner surfaces of the chamber lined with cardboard and the chamber evacuated, the scattered radiation was certainly reduced to a low value.

In the front screen determination the film was situated in a strong magnetic field so that any electrons that were ejected backward from the film were curved back into it and caused an increase in density. This effect certainly contributes some error but it should be small since comparatively few electrons are ejected backward. In the arrangement used in determining the effect of the film alone, the larger size of the apparatus made it possible to provide magnetic shielding for the region of the film, and thereby largely prevented an increase in density due to any curving-back effect.

Since the film had to be removed from the front screen by a finite distance for the front screen and the film alone effects, an indeterminate error was introduced. In the case of the front screen effect, while it was possible to extrapolate the curves of Figs. 5 and 9 to a 0 cm. separation, no proof could be obtained, owing to the lack of a sufficiently powerful magnetic field, that the curve continued as was assumed.

A further error is introduced by calculating the percentage effects as though the density versus exposure factor curves were linear, whereas they are slightly curved in the region used.

Discussion and Summary of Results

Table II gives a summary of the effects of the front and of the back screens, and of the film alone, for both lead screens and Patterson screens. The fact that the three effects add up to more than 100% in itself indicates the magnitude of the joint errors involved.

TABLE II

SUMMARY OF ALL THE RESULTS FOR LEAD SCREENS AND PATTERSON SCREENS

	Lead screens	Patterson screens
Exposure factor used	55	45
Maximum density	2.21	2.20
Front screen effect:		
(a) Due to electrons, %	51.2	42.5
(b) Due to light energy, %	0.0	9.8
(c) Total effect, %	51.2	52.3
Back screen effect, %	49.0	47.8
Film alone effect, %	3.6	3.4
Total	103.8	103.5

No check on the percentage of the Patterson back screens effect due to light energy could be obtained. However, it seems a safe assumption to say that it is of the same order of magnitude as that for the front screen.

The effects reported here were obtained for only one thickness of lead screens and one type of Patterson screen, and for one thickness of brass. It is probable that if these factors were changed the same general type of results would be obtained.

It is obvious from this table that the use of some form of intensifying screen is imperative in gamma radiography. That the effect of the film alone should be so small is understandable when it is realized that the only way in which gamma rays can cause darkening is by the ejection of electrons, and only those electrons having paths largely within the emulsion will produce any appreciable effect. Since the absorption by the film of gamma rays is small, comparatively few electrons are available for darkening. It is doubtful whether this fact has been fully appreciated by film manufacturers or users. The absorption of the gamma rays by the film could be increased if materials of high atomic number were incorporated in the emulsion. The fact that most of the darkening comes from the effects of the front and back screen is indicative of the care that should be taken in the choice of these screens.

The practical aspects of the choice of these screens from the point of view of the sensitivity obtainable and the intensification that can be secured has been discussed by some of the authors in another publication (1). It will suffice to state here that the screens should be maintained in firm contact with the film so that the electrons ejected from the screen will affect the film at their point of origin, rather than at a considerable distance, to avoid loss of sharpness. In the second place the screens should be clean. If a small section of the screen is covered with some foreign material, the latter will absorb the electrons from the screen and will produce only a smaller number of electrons owing to its own absorption of the gamma rays. This will result in a light spot on the film.

Acknowledgments

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ON THE EXTENDED USE OF KLEINLOGEL'S RAHMENFORMELN¹

BY I. F. MORRISON²

Abstract

This paper contains but a single idea. Its purpose is to show how, by the use of Kleinlogel's Rahmenformeln, the number of simultaneous linear equations that occur in the analysis of indeterminate structures can be reduced materially by using a primary structure, itself made up of indeterminate parts, provided the bending moment diagrams can be drawn for them. These are obtained from the Rahmenformeln. In order to recall to the reader's mind the well known moment-area method a brief summary of that process is included. A practical numerical example of the analysis of a frame indeterminate to the seventh degree is worked out in detail. Two arrangements of the indeterminate components are chosen in the illustrative example. The final bending moment diagram is shown for a simple loading case and the influence line for the bending moment at one point is discussed briefly.

Introduction

During the recent war the Eighth Edition of Professor Kleinlogel's well known Rahmenformeln was reprinted in the United States by the authority of the Alien Property Custodian. It was published by Frederick Ungar Publishing Co. in 1943, supplemented with a crib in English—published separately—for the benefit of those not familiar with the German language.

This remarkable book contains diagrams and formulae for simple frames of various shapes, support conditions, and loadings. One hundred and fourteen frames are listed with 1643 diagrams accompanied by numerous formulae. The diagrams show the moment-curves for each case of loading; the formulae give the algebraic expressions for the moments, shears, and reactions. The index of contents is an odd one consisting, as it does, of a series of simple illustrations showing the shape and support conditions of each frame with the numbers of the pages on which the moment-curves and formulae pertaining to it will be found. A very brief introduction contains all the necessary information concerning notation, rules for signs, and other pertinent information. However, one does not need to be able to read this part to make use of the tables, which are quite obvious as to meaning. Besides, the English translation now available obviates this difficulty.

At first sight, one might think that this useful handbook would be limited in its application to only those cases contained in it. This is, however, a false conclusion for, although it is not so indicated in the introduction, the simple frames can be used as units with which to build up multiple frame structures of unlimited extent. By such synthesis, the use and value of the book becomes considerably extended and it is the purpose of this paper to

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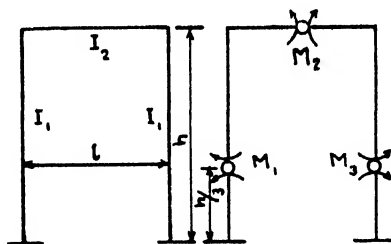
present a method by which the analysis of multiple frame structures may be carried out in a simple and direct manner based on the information contained in it.

This method, namely, the moment-area method, consists in dissociating the multiple frame into units that can be found in the text and in using these units as the elements of a primary structure. The elements themselves are statically indeterminate, but, since the analysis for them is already at hand in the text, no difficulty by way of preliminary analysis is present and the synthesis is carried out with these statically indeterminate units instead of the statically determinate units usually used for that purpose. The amount of effort required to analyze a highly indeterminate structure is enormously reduced and for that reason the analysis of multiple structural frames, which might appear as formidable, is brought within quite reasonable range.

The Moment-area Method

The purpose of this section is to recall to the mind of the reader the moment-area method.

In order to demonstrate this most useful, perhaps, of all methods of structural analysis, a simple algebraic example will be given. Consider a rigid frame as shown in Fig. 1 with which the reader will be undoubtedly quite familiar.



FIGS. 1 and 2.

This structure is indeterminate to the third degree, i.e., three unknown, or redundant, reactions in addition to the three reactions of plane statics are present, and, therefore, in addition to the three equations of equilibrium of plane statics, three additional equations in terms of the three redundants must be established. These form a system of independent, simultaneous, linear equations that must eventually be solved. The moment-area method is one that sets up these equations; it does not offer a method of solution of them. When they are few in number the solution of them can be easily and quickly accomplished.

The first step in the process is to render the indeterminate structure determinate by the insertion of suitable cuts and hinges. In the present case, this is shown in Fig. 2, in which three hinges have been inserted. The structure is now statically determinate and stable. This is called the "primary structure".

From the equations of virtual-work, the set of simultaneous equations involving the redundants M_1 , M_2 , and M_3 , the unknown moments at the selected points of the indeterminate structure, are readily established. These may be written in condensed form as

$$\sum a_{ij} M_j = c_i \quad i \text{ 1 to 3}$$

$$a_{ij} = a_{ji} \quad j \text{ 1 to 3}$$

The c_i are the loading terms. It is easily shown that the a_{ij} are given by the "work equation" owing to a self-stressed condition. The most important

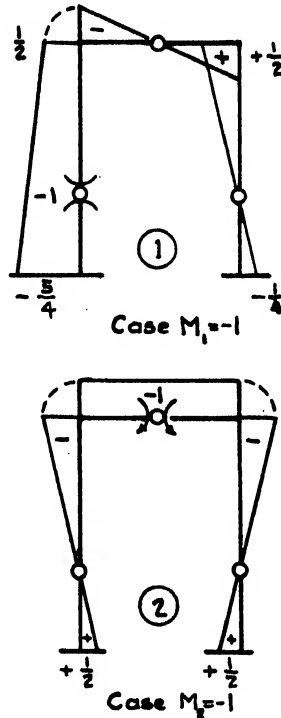


FIG. 3.

term in the complete work equation and the only one usually retained, but not necessarily so, in analysis of this sort is

$$a_{ij} = \sum \int_0^l \frac{M_i M_j ds}{EI}$$

In this equation, the M_i and the M_j are the bending moments in each member due to a self-stressed condition imposed by placing successively at each hinge a couple, -1 . The EI is the product of the modulus of elasticity by the moment of inertia of the cross section for each member. Since E is often constant and occurs on both sides of the equation, it will be assumed to

disappear from the following equations. The integration is taken over the length of each member and the summation sign indicates that the sum of these integrations must be taken.

This process requires three bending moment diagrams, two of which are shown in Figs. 3, (1), and 3, (2), respectively. The third is like 3, (1) except reversed. The areas so displayed on the diagrams are called moment-areas and the method takes its name from this fact.

The simple integrations for many cases have been worked out and are given in a table in Müller-Breslau's *Die Graphische Statik der Baukonstruktionen*, Band II, 2 abt. page 56. Many combinations of moment-areas are included in this table but here only one will be given which is all that is necessary for the present purpose.

Fig. 4 indicates the case referred to and shows two trapezoidal moment-areas that are to be multiplied and integrated from 0 to l . The factor $\frac{1}{EI}$

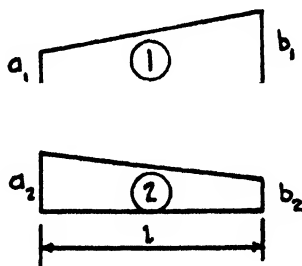


FIG. 4.

will be considered constant for the member and, therefore, omitted in the integration. Then

$$\frac{1}{EI} \int_0^l M_1 M_2 ds = \frac{l}{6EI} [a_1(2a_2 + b_2) + b_1(a_2 + 2b_2)].$$

The moment-areas 1 and 2 may be said to be "paired" by this process. The matrix a_{ij} , so to speak, represents the structure in mathematical form and might be called the "structure". It depends, however, on the choice of the primary structure. Owing to the assumptions of Hooke's law and elasticity of the members of the structure, the matrix is of necessity always symmetric.

Returning to the analysis, we have now to work out the six constants a_{ij} by pairing the moment-areas for the frame.

As a sample calculation, take a_{12} .

Starting with the left leg of the frame,

$$\int_0^l M_1 M_2 ds = -\frac{h}{6} \cdot \frac{3}{2} = -\frac{h}{4},$$

and proceeding around the frame, one finds

$$a_{12} = -\left(\frac{h}{4I_2} + 0 + \frac{h}{4I_2}\right) = -\frac{h}{2I_2}.$$

In the same way, all the other coefficients may be set down, practically by inspection. Thus, we have:

$$\begin{aligned} a_{11} &= \frac{7}{8} \frac{h}{I_2} + \frac{1}{12} \frac{l}{I_1} & a_{22} &= +\frac{l}{I_1} & a_{33} &= \frac{7}{8} \frac{h}{I_2} + \frac{1}{12} \frac{l}{I_1} \\ a_{12} &= -\frac{h}{2I_2} & a_{23} &= -\frac{h}{2I_2} & a_{31} &= -\left(\frac{1}{8} \frac{h}{I_2} + \frac{1}{12} \frac{l}{I_1}\right) \end{aligned}$$

It is customary to indicate the ratio of the moment of inertia of a member to its length by a single letter, called the "stiffness factor." Here, however, we shall put $k = \frac{I_1}{I_2} \cdot \frac{h}{l}$, which is in concordance with Kleinlogel's formulae.

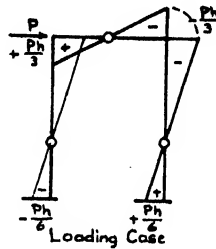


FIG. 5.

The loading terms are determined also from the moment-area of the primary structure, due to any specified loading on it, paired with each of the three self-stressed moment-areas. If, for example, the loading as shown in Fig. 5 be chosen, then

$$C_1 = -\frac{Ph}{12} \cdot \frac{h}{I_2} - \frac{Ph}{12} \cdot \frac{l}{I_1}$$

$$C_2 = +\frac{Ph}{6} \cdot \frac{h}{I_2}$$

$$C_3 = +\frac{Ph}{12} \cdot \frac{h}{I_2} + \frac{Ph}{12} \cdot \frac{l}{I_1}$$

The equations then become, in matrix form,

$$\begin{bmatrix} \frac{7}{8}k + \frac{1}{12}, & -\frac{k}{2}, & -\frac{1}{8}k - \frac{1}{12} \\ -\frac{k}{2}, & 1, & -\frac{k}{2} \\ -\frac{1}{8}k - \frac{1}{12}, & -\frac{k}{2}, & \frac{7}{8}k + \frac{1}{12} \end{bmatrix} \cdot \begin{bmatrix} M_1 \\ M_2 \\ M_3 \end{bmatrix} = \begin{bmatrix} -\frac{Ph}{12}(k+1) \\ +\frac{Ph}{6}k \\ +\frac{Ph}{12}(k+1) \end{bmatrix}$$

This completes the demonstration, for there is no point in solving these algebraic equations. The object has been merely to show how they are set up by means of the moment-area method. Of course, it is much more expedient to work directly with the numerical values.

Solution of the Equations

The main difficulty that arises in any method of analytical analysis of a highly indeterminate structure is in the solution of the large set of simultaneous equations that arise in the process. This becomes very tedious and great care is required in checking the solution as it progresses. For this reason any method by which the number of equations can be reduced offers a material advantage.

There are a number of methods that have been developed by which the number of simultaneous equations can be reduced. The present paper presents such a method. It is based, however, on the assumption that the moment-area diagrams for a number of simple, though statically indeterminate, frames are readily at hand as mentioned in the introduction. Kleinlogel's Rahmenformeln provides this information.

The Use of Kleinlogel's Rahmenformeln

We now turn to the use of Kleinlogel's diagrams. In the preceding moment-area method, the primary structure was chosen as statically determinate solely because it was easy to construct the bending moment diagrams for such a structure. In the Rahmenformeln, however, we have access to literally hundreds of cases of simple, indeterminate frames. Instead, then, of rendering the statically indeterminate structure determinate, to obtain a tractable primary structure, we may adopt a primary structure made up of frames the moment-areas of which are already known and therefore also easily handled.

This method of dissociating the structure into a primary structure, itself composed of indeterminate parts, reduces very materially the number of simultaneous equations to be solved, as will be seen in the following examples.

Numerical Examples

In order to illustrate the advantage so gained by this process, it is proposed to analyze the relatively simple structure shown in Fig. 6, *a*. First, the primary structure is decided upon. This may be done in several ways. In this case, the choice is shown in Fig. 6, *b*. The original structure is indeterminate to the seventh degree. By inserting two hinges as shown, the primary structure is indeterminate to the fourth degree.* In selecting the primary structure care must be exercised to select only such an arrangement of hinges or cuts as will leave the elements of the primary structure such that the moment-area diagram is already known. It should be noted that the shorten-

* The left-hand hinge is on a horizontal shelf, so to speak, and removes two constraints. The right-hand hinge removes only one constraint.

ing of the posts is assumed to be neglected as usual and, as a consequence, there will be no vertical displacement of the hinges. The solution is approximate in this respect.

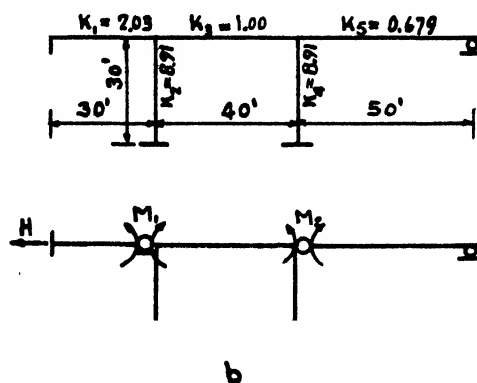


FIG. 6.

The values of k shown in Fig. 6, *a*, have been obtained by first selecting one value of the stiffness factor as a unit value and then finding the ratios of it to the respective stiffness factors of the remaining members. In the present case the girder of the center span was so chosen that $k_3 = \frac{I_3}{I_3} = 1$. Each pairing of the moment-areas is multiplied by the corresponding k -value for the member.

Since the structure is indeterminate to the seventh degree we would, if the primary structure were rendered determinate as in the usual procedure, have to determine $\frac{n(n+1)}{2} = 28$ independent coefficients, and $n = 7$ loading terms; in itself a formidable task. Then seven simultaneous linear equations would have to be solved; this is time consuming, to say the least.

By using the primary structure as composed of elements, themselves indeterminate, the number of equations to be solved has been reduced to three and the number of coefficients to six, thus effecting a very large saving of effort.

In any case, to determine the number of redundants, let n be the degree of indeterminateness of the structure and N the sum of the degrees of indeterminateness of the components of the primary structure, then the number of redundants, say R , is

$$R = n - N.$$

In the present case, the left-hand girder is indeterminate to the first degree*, the middle frame to the third degree, and the right-hand girder to the zero degree. Thus,

$$R = 7 - 4 = 3,$$

* Note that the right-hand end of it is on a roller supported by the post.

which is the number of redundants selected and shown in Fig. 7 as M_1 , M_2 , and H . The arrows indicate the positive directions of the forces and couples.

Figs. 7, (1), (2), (3) show the moment-areas for the structure as obtained from the Rahmenformeln for the self-stressed conditions $M_1 = -1$, $M_2 = -1$, $H = -1$,* respectively. By pairing the diagrams, as already explained, the

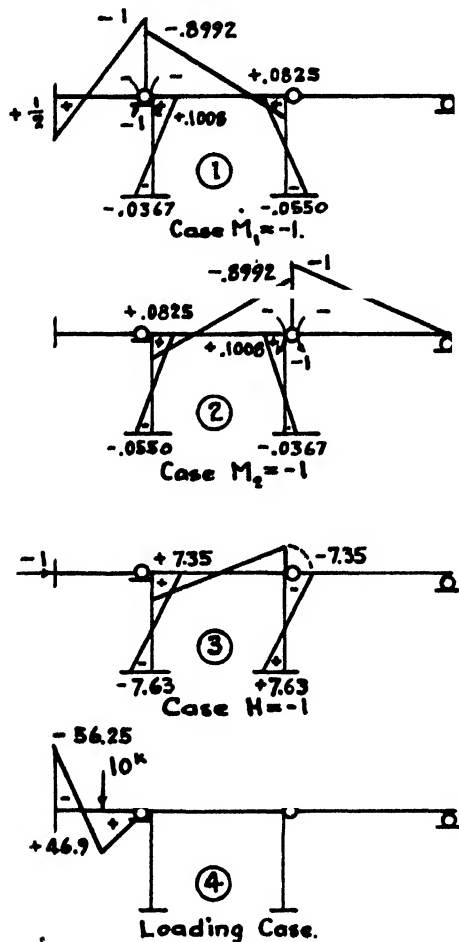


FIG. 7.

numerical coefficients are easily obtained. They are shown as elements of the matrix.

The equations have been solved for the simple case of loading shown in Fig. 7 (4). The reciprocal matrix for three equations is very easily obtained and once set down serves for all possible cases of loading and temperature changes.

* Actually H is the connecting force, at the right-hand end, of the left span to the center span.

$$\begin{bmatrix} 0.7927 & 0.1223 & -1.226 \\ 0.1223 & 0.5115 & 1.226 \\ -1.226 & 1.226 & 352.7 \end{bmatrix} \cdot \begin{bmatrix} M_1 \\ M_2 \\ H \end{bmatrix} = \begin{bmatrix} -19 \\ 0 \\ 0 \end{bmatrix}$$

$$\begin{array}{rcl} M_1 & 178.9 & -44.64 & 0.7770 & -19 \\ M_2 & \begin{array}{c} 1 \\ 135.4 \end{array} & -44.64 & 278.1 & -1.122 & 0 \\ H & 0.7770 & -1.122 & 0.3905 & 0 \end{array}$$

$$M_1 = -\frac{3397.77}{135.3} = -25.1^{ft.k}$$

$$M_2 = +\frac{849.55}{135.3} = +6.27^{ft.k}$$

$$H = -\frac{14.763}{135.3} = -0.109^k$$

The final bending moment diagram for the loading chosen is shown in Fig. 8. The bending moment diagrams of Fig. 7 are used to determine the bending moment diagrams of Fig. 8.

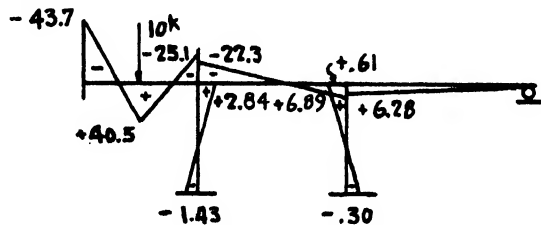


FIG. 8.

A second analysis of the same structure in which a cut has been made at the middle of the center span is shown in Figs. 9 and 10. The equations

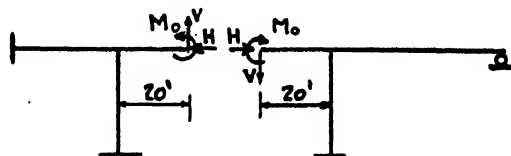


FIG. 9.

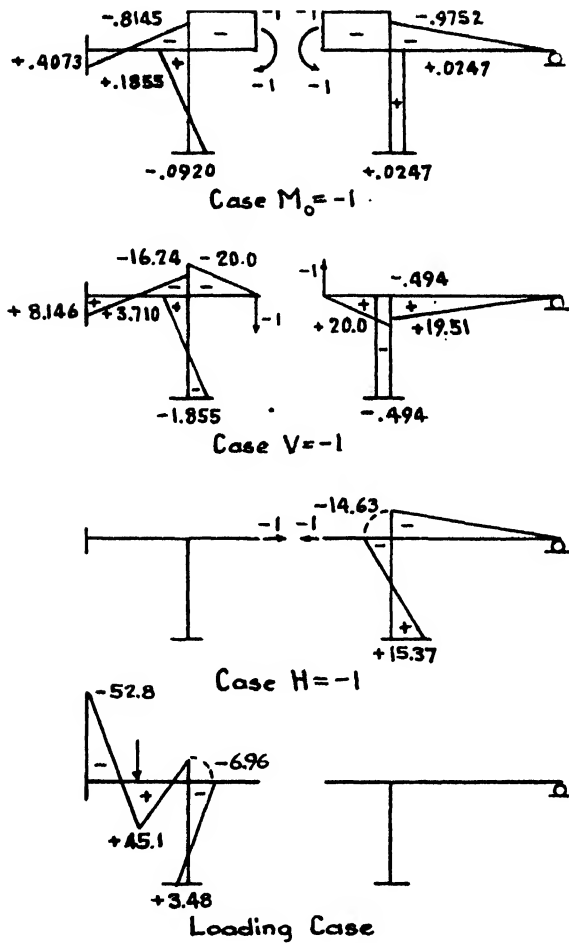


FIG. 10.

follow and the results shown in Fig. 11 check within reason those of the first analysis. All the numerical work, except for the final reciprocal matrix, was carried out on an ordinary slide rule.

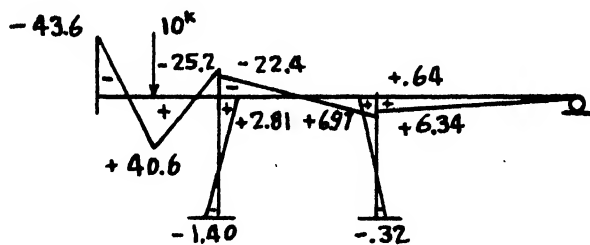


FIG. 11.

$$\begin{bmatrix} 1.632 & 3.814 & 3.309 \\ 3.814 & 385.9 & -66.18 \\ 3.309 & -66.18 & 718.4 \end{bmatrix} \cdot \begin{bmatrix} M_0 \\ V \\ H \end{bmatrix} = \begin{bmatrix} -15.5 \\ -310.0 \\ 0 \end{bmatrix}$$

$$\begin{array}{cccc|c} M_0 & & 272.9 & -2.959 & -1.529 & -15.5 \\ V & 1 & -2.959 & 1.162 & 0.1206 & -310.0 \\ & 428.9 & & & & \\ H & & -1.529 & 0.1206 & 0.6152 & 0 \end{array}$$

$$M_0 = -7.72^{ft.k}$$

$$V = -0.733^k$$

$$H = -0.0319^k$$

In cases of symmetrical structures, advantage should be taken of the symmetry that can be maintained by suitable choice of cuts or hinges. Also the method of group loadings can be used to advantage wherever group loadings tend to simplify the moment-area diagrams. By group loadings is meant the choice of two or more unit loads, or couples, applied to the primary structure simultaneously to produce a self-stressed condition. This method, however, does not reduce the number of redundants.

The method of the elastic center can be applied also by making the a_{ij} , $i \neq j$ coefficients equal to zero, but a preliminary investigation shows that, except in the case of symmetrical structures, there is little, if any, advantage to be gained by it.

Influence Lines

If further detailed study of the structure be required, influence lines should be drawn. This can be done by setting up the equations of the influence line for any chosen item that requires detailed attention.

As an illustration, let it be required to draw the influence line for M_1 . In the solution, only the loading terms will change; therefore, the equation for M_1 will be, from the reciprocal matrix,

$$M_1 = 1.325C_1 - 0.331C_2 + 0.00574C_3, \quad (1)$$

in which the C 's are to be determined by pairing the moment-area diagram for the unit load with each of the moment-area diagrams for the three self-stressed conditions.

The moment-area diagrams for the unit load in each span successively are shown in Fig. 12. There will be one equation for each span. For Case *a*, only C_1 will be present and for Case *c*, only C_2 . For Case *b*, however, all three values of C will exist.

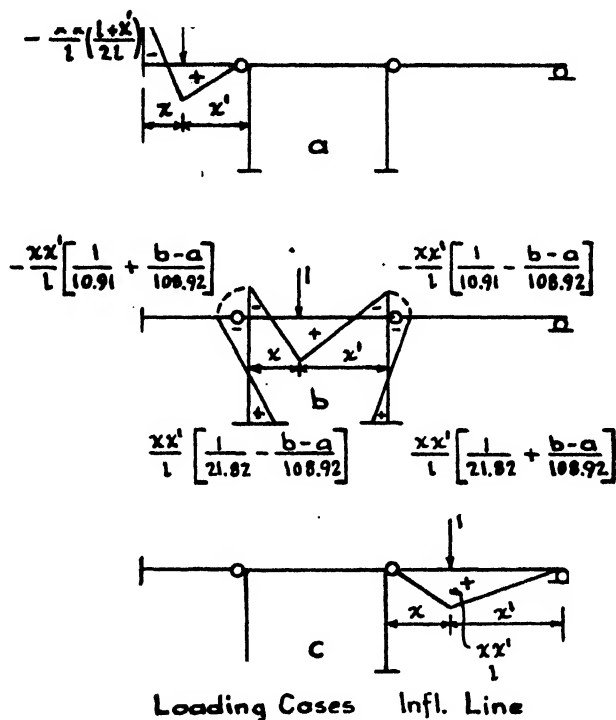


FIG. 12.

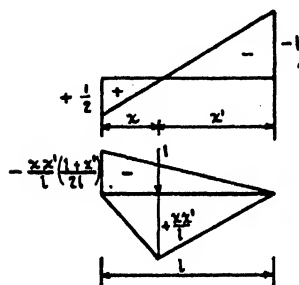


FIG. 13.

In order to express the position of the moving unit load, we shall take it at a distance x from the left-hand end of each span, and x' from the right-hand end. For the unit load on the left-hand span C_1 can be most readily obtained from Fig. 13. Thus, from pairing the moment-areas shown, we find

$$C_1 = \frac{-2.03x^2x'}{4l^2}$$

In a similar way we obtain for the center and the right-hand spans respectively

$$C_1 = \frac{xx'}{l} (-0.1107 - 0.1506b + 0.0146a)$$

$$C_2 = \frac{xx'}{l} (-0.1107 - 0.1506a + 0.0146b)$$

$$C_3 = \frac{xx'}{l} 1.225 (b - a),$$

and

$$C_2 = \frac{-0.1132 xx'}{l^2} (l + x'),$$

in which

$$\frac{x}{l} = a, \quad \frac{x'}{l} = b.$$

Inserting these values of C in Equation (1), we find for the three spans, respectively,

$$M_1 = -20.2 a^2 b$$

$$M_1 = -7.33 ab - 7.85 ab^2 + 2.49 a^2 b$$

$$M_1 = +1.87 (a^2 b + ab^2)$$

The plotted influence line is shown in Fig. 14.

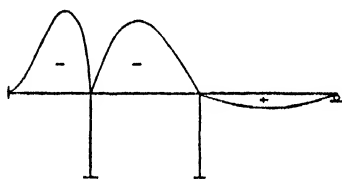


FIG. 14.

PRECISION OF HEAT-TRANSFER MEASUREMENTS WITH THERMOCOUPLES—INSULATION ERROR¹

W. A. MOHUN²

Abstract

A method has been developed for calculating the temperature variation in insulated thermocouple lead wires that do not follow an isothermal path. The difference between the temperature of the junction and that of the surrounding material that it purports to measure has been called "insulation error." It has been shown that insulation error is determined by variations in the temperature of the path followed by the lead wires only over a limited distance from the junction, which has been called the "critical distance." Hence, to eliminate insulation error the path of the wires need be isothermal only for the critical distance. A simple method has been developed for calculating the critical distance and the insulation error. When the path of the wires cannot be made isothermal the conditions for minimum experimental error are shown to be small diameter wires of low specific conductivity with a minimum of insulation.

The determination of fluid film heat transfer coefficients requires the measurement of the surface temperature of the tube or other dividing wall through which heat is being transferred. This usually requires that a thermocouple be embedded in the tube wall and the surface temperature calculated from the temperature indicated by the couple.

In a previous paper (1) the effects of geometric errors in determining the location of the thermocouple tip with respect to the tube surface were analyzed and methods of minimizing them were described. The other major source of error in such systems may be termed "insulation error" since it occurs when *insulated* lead wires are carried away from the junction along a path that is not isothermal. Heat is then transmitted to, or from, the junction along the wire itself so that the temperature of the junction is actually different from that of the material surrounding it. It has long been recognized qualitatively that the lead wires should be brought out along an isothermal path. But in practice it is not usually possible to adhere strictly to this condition, particularly in the case of tubes, for which chordal holes are preferably employed. It is hoped that the present quantitative analysis will help investigators, not only to estimate the magnitude of errors that cannot be avoided, but more particularly to choose experimental arrangements that will minimize these errors.

Qualitative Discussion

It is convenient to discuss the problem first in terms of a single insulated wire completely embedded in solid metal (e.g., in a low-melting solder) in a chordal hole in a tube wall, such as that in Fig. 1.

Heat will be flowing radially through the tube wall and the temperature gradient within the wall will depend on the density of heat flux and on the

¹ Manuscript received July 8, 1948.

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thermal conductivity of the wall. Table I shows that the temperature gradient in the wall may be quite steep and that the temperature difference across the width of a fine thermocouple lead wire may amount to several

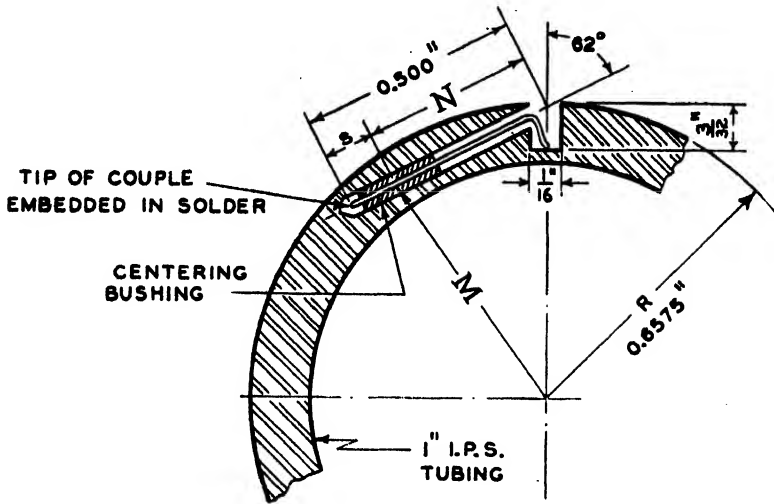


FIG. 1. Sketch of thermocouple installation.

TABLE I
TEMPERATURE GRADIENTS THROUGH METAL WALLS

Metal	k at 400° F.*, B.t.u./ (hr.) (sq. ft.) (° F./in.)	Heat flux, B.t.u./ (hr.) (sq. ft.)	Temp. gradient ° F./in.	Temp. difference (° F.) across	
				1 in. I.P.S. wall†	No. 30 B & S wire‡
Copper	2605	400,000	153	20.4	1.6
		200,000	77	10.2	0.8
		100,000	38	5.1	0.4
		50,000	19	2.6	0.2
Aluminum	1560	400,000	256	34.0	2.7
		200,000	128	17.0	1.3
		100,000	64	8.5	0.7
		50,000	32	4.2	0.3
Yellow brass	1010	400,000	396	52.6	4.2
		200,000	198	26.3	2.1
		100,000	99	13.2	1.0
		50,000	50	6.6	0.5
Steel	300	200,000	667	88.7	7.0
		100,000	334	44.4	3.5
		50,000	167	22.2	1.8

* Kent, "Mechanical Engineers' Handbook", Vol. I, 3-28.

† Thickness = 0.133 in.

‡ Thickness = 0.0105 in.

degrees. As a result of this temperature difference across the wire, heat will flow through the insulation into the wire, across the wire, and out again through the insulation on the other side. Because of the high thermal resistance of the electrical insulation, the amount of heat that takes this path will be small relative to the flux through the tube wall itself, but it may not be negligible. Furthermore, if the wire is not isothermal along its length, some of the heat that enters through the insulation at a given point will flow along the wire before passing out through the insulation on the other side. The components of flow across the wire and along the wire may be considered separately. The former component is not of major importance in the present discussion as it does not alter the temperature of the wire, but the component along the wire causes the temperature of the wire to differ from that of its immediate surroundings, and is the cause of insulation error.

The first conclusions of importance will be made clear by reference to Figs. 2 and 3, which illustrate a wire subjected only to a transverse component of heat flux. Fig. 2 shows a cross section of the tube and wire in the plane

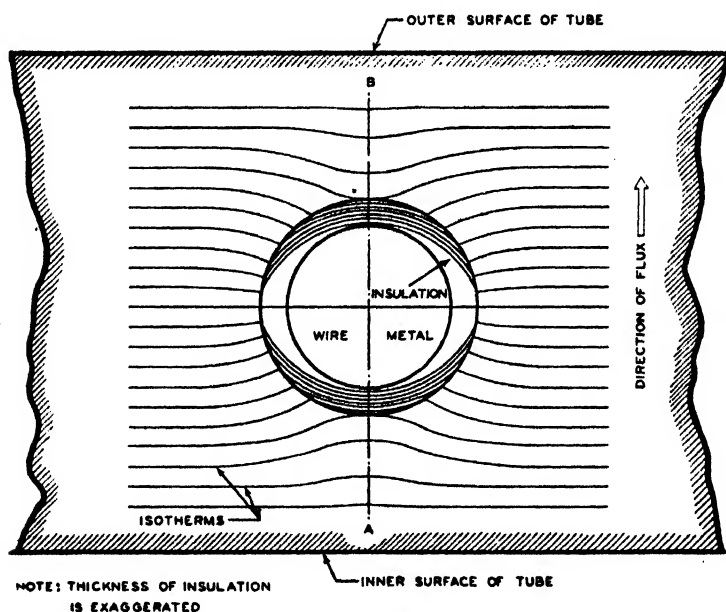


FIG. 2. Enlarged cross section of tube in plane of heat flux showing distortion of isotherms by insulated wire—for case of no longitudinal heat flux.

of the heat flux; this is a longitudinal section in the case of the tube; for simplicity throughout this paper it will be assumed to be a right cross section in the case of the wire, although strictly speaking the axis of the wire is not necessarily normal to the radii of the tube, so that cross sections of the wire in the plane of the heat flux may actually be slightly elliptical in shape. This figure illustrates roughly how the isotherms, normally parallel, are

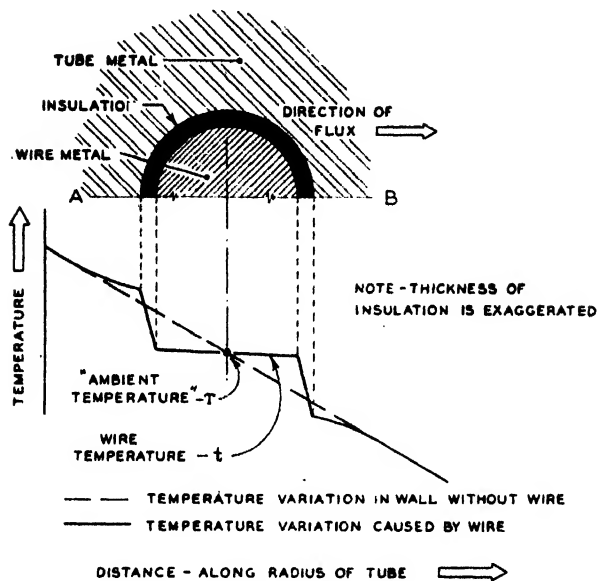


FIG. 3. Temperature variation across wire—for case of no longitudinal heat flux.

distorted in the region of the wire. Temperatures along the line AB of Fig. 2, a line which passes through the center of the wire, are plotted against distance in Fig. 3. From these figures we may draw two conclusions:

(a) The temperature drop is so largely concentrated in the insulation that the temperature of the wire metal may be considered essentially constant across any given cross section taken in the direction of heat flow; this wire temperature at any given point will be called t . Then let T be the temperature that would have obtained in the metal wall at the same point (corresponding to the center of the wire) if the wire had not been there. This "would-have-been" temperature is the average of the actual temperatures existing in practice on the two sides of the wire (see Fig. 3), and, since it is thus the average temperature to which the periphery of the wire at any cross section is subjected, it will be termed the *ambient* temperature.

(b) Assuming that the cross section of the wire and its insulation is symmetrical and that the temperature gradient in the surrounding metal wall is uniform, we see from Fig. 3 that $t = T$ when there is no longitudinal distribution of heat.

But when the wire is not brought out along an isothermal path, heat flows along the wire as well as across it, and t is no longer equal to T . Then at the tip of the wire (i.e., at the junction):

$$\text{Insulation error} = t_0 - T_0. \quad (1)$$

Insulation Temperature Drop

At any given cross section of the wire, the temperature of the outer surface of the insulation varies from a maximum on the side nearest the inside of the tube to a minimum on the side nearest the outside of the tube. Since the temperature variation in the tube wall is linear with distance if one neglects distortion of the isotherms in the immediate region of the wire, the projection of the peripheral temperature on the diameter will, to a first approximation, also be linear with distance (see Fig. 4, and compare with Fig. 3). In Fig. 4,

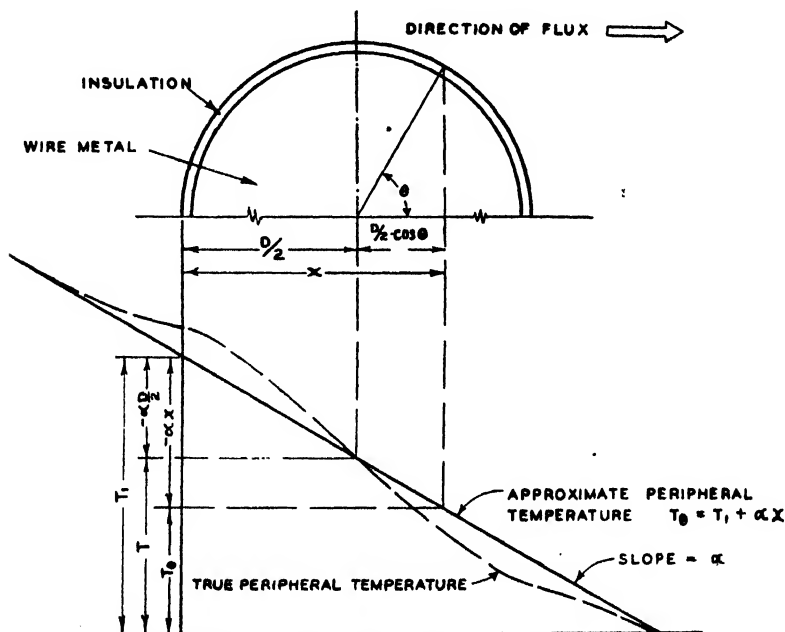


FIG. 4. Calculation of peripheral temperature.

x is distance measured across the diameter of the wire from the hotter side, α is the temperature gradient in the tube wall,* and T_θ is the temperature at any point on the periphery of the wire. From the geometry of Fig. 4 it follows that

$$T = T_1 + \frac{\alpha D}{2} ; \quad (2)$$

and,

$$T_\theta = T_1 + \frac{\alpha D}{2} + \frac{\alpha D}{2} \cos \theta . \quad (3)$$

Since the temperature of the wire metal may be considered essentially constant throughout the cross section, the temperature difference across the insulation at any point around the periphery is

$$\Delta T_i = T_\theta - t . \quad (4)$$

* Since the temperature decreases in the positive direction of x , α is negative.

This temperature difference ΔT_i is not constant around the wire, but varies from a maximum positive value at one side of the wire to a maximum negative value at the other side. When the positive and negative values of ΔT_i are symmetrical and equal, the quantities of heat entering and leaving the wire at the cross section are equal and there is no flow of heat along the wire. When the positive and negative values are not equal, the effective ΔT_i causing a net flow of heat into the wire is the average value of ΔT_i taken around the periphery of the wire; that is,

$$\overline{\Delta T_i} = \frac{1}{\pi} \int_0^\pi \Delta T_i \cdot d\theta. \quad (5)$$

Substituting from Equations (4) and (3), integrating, and then substituting Equation (2):

$$\overline{\Delta T_i} = T - t. \quad (6)$$

That is, the average temperature difference causing a net flow of heat into, or out of, the wire at any given cross section is simply the difference between the ambient temperature and the temperature of the wire.

It can be seen intuitively that Equation (6) is not restricted to the hypothetical case in which T_θ is a linear function of x ; the integration will give the same result provided only that T_θ is symmetrical with respect to T at the center of the wire. This condition, and hence Equation (6), may be assumed to be approximately true at any cross section of the wire (see dotted curve in Fig. 4), although this condition is rigorously true only in the limiting case when the fluxes entering and leaving the wire at the same cross section are equal, i.e., when there is no longitudinal flux and t equals T , as illustrated in Fig. 3.

Wire Temperature Equation

In order to obtain an expression defining the temperature of the wire metal at any point, consider an increment of the wire taken as a right cross section, ds inches thick, at a distance s from the tip, as shown in Fig. 5. In general, the direction of increasing temperature in the wire metal will be the same as the direction of increasing ambient temperature, since it is the change in ambient temperature that causes change in wire temperature. The ambient temperature will be some function of s , and for convenience the temperature datum will be taken as zero ambient temperature at the tip of the wire. Consider the flow of heat Q through the cross section at s into the part of the wire to the left of the section as the positive direction of heat flux, since this has been arbitrarily defined in Fig. 5 as being the direction of decreasing wire temperature.

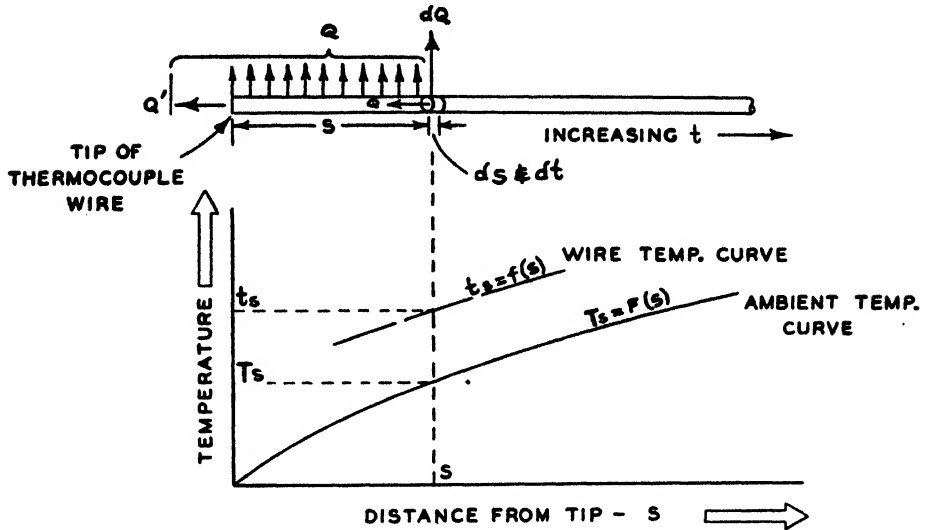


FIG. 5. Calculation of wire temperature equation for known ambient temperature curve.

Then according to Newton's law the flow of heat across the increment is given by

$$Q = -K \cdot \frac{\pi D^2}{4} \frac{dt}{ds}, \quad (7)$$

where the symbols are as defined in the Table of Nomenclature.

Since the flow of heat out through the surface of the increment is

$$dQ = \frac{k}{w} \cdot \pi D \cdot ds(T - t), \quad (8)$$

the heat lost through the surface and end of the wire will be

$$Q = \int_0^s dQ + Q'$$

$$\frac{k \pi D}{w} \int_0^s (T - t) ds + \frac{k}{w} \cdot \frac{\pi D^2}{4} (T_0 - t_0). \quad (9)$$

Since heat is not stored in any part of the wire, we may equate (7) and (9), and noting that $T_0 = 0$ by definition we obtain

$$\int_0^s \phi \cdot T \cdot ds - \int_0^s \phi \cdot t \cdot ds - \frac{k t_0}{wK} = - \frac{dt}{ds}, \quad (10)$$

where $\phi = \frac{4k}{wKD}, \quad (10a)$

and dt/ds is the temperature gradient in the wire at s .

Equation (10) defines the curve $t = f(s)$ giving the temperature of the wire at any point. In practice ϕ may differ for different regions along the length of the wire, so it is best to keep it inside the integral sign.

Since the heat Q' lost through the end of the wire may usually be neglected, as will be shown later, Equation (10) may be written

$$\int_0^s \phi \cdot T \cdot ds - \int_0^s \phi \cdot t \cdot ds = - \frac{dt}{ds} \quad (11)$$

And for a value s' corresponding to a maximum or a minimum in the curve $t = f(s)$, we have

$$\int_0^{s'} \phi \cdot T \cdot ds - \int_0^{s'} \phi \cdot t \cdot ds = 0 \quad (12)$$

Equation (12) indicates that the wire may be considered divided into separate regions by the maxima and minima in the t curve, and that temperature effects in one region do not carry over into the next. It is also evident that the maxima and minima in the curve $t = f(s)$ coincide with the maxima and minima in the curve $T = F(s)$ since the variations in t are due solely to the variations in T and hence must always be in the same sense as those in T . This generalization is helpful in plotting the wire temperature curve, and makes Equation (12) applicable where s' is defined by the maxima and minima in the ambient temperature curve.

Equation (11) cannot be solved directly to determine the wire temperature curve, but Equations (11) and (12) provide the criteria by which we may check any wire temperature curve obtained by trial and error or approximate methods.

Approximate Solution

An approximate solution of Equation (10), sufficiently accurate for all practical purposes, may be obtained by converting it to the approximate form

$$\int_0^s \phi \cdot T \cdot ds - \sum_0^n \phi \cdot \bar{t} \cdot \Delta s - \frac{k t_0}{wK} = - \frac{\Delta t_n}{\Delta s_n} \quad (13)$$

where \bar{t} is the average value for each increment concerned.

If each increment is assumed to be sufficiently small that the variation in t across it may be considered linear with distance, we may write

$$\bar{t}_n = t_{n-1} + \frac{\Delta t_n}{2} \quad (14)$$

for any increment. Using Equation (14), the second term of Equation (13) may be broken up into some of its constituent increments, so that Equation (13) becomes

$$\begin{aligned} \int_0^s \phi \cdot T \cdot ds - \sum_0^{n-2} \phi \cdot \bar{T} \cdot \Delta s - \phi_{n-1} \cdot \Delta s_{n-1} \left(t_{n-2} + \frac{\Delta t_{n-1}}{2} \right) \\ - \phi_n \cdot \Delta s_n \left(t_{n-2} + \Delta t_{n-1} + \frac{\Delta t_n}{2} \right) - \frac{k t_0}{wK} = - \frac{\Delta t_n}{\Delta s_n} \end{aligned} \quad (15)$$

The significance of the various subscripts will be made clear by reference to Fig. 6.

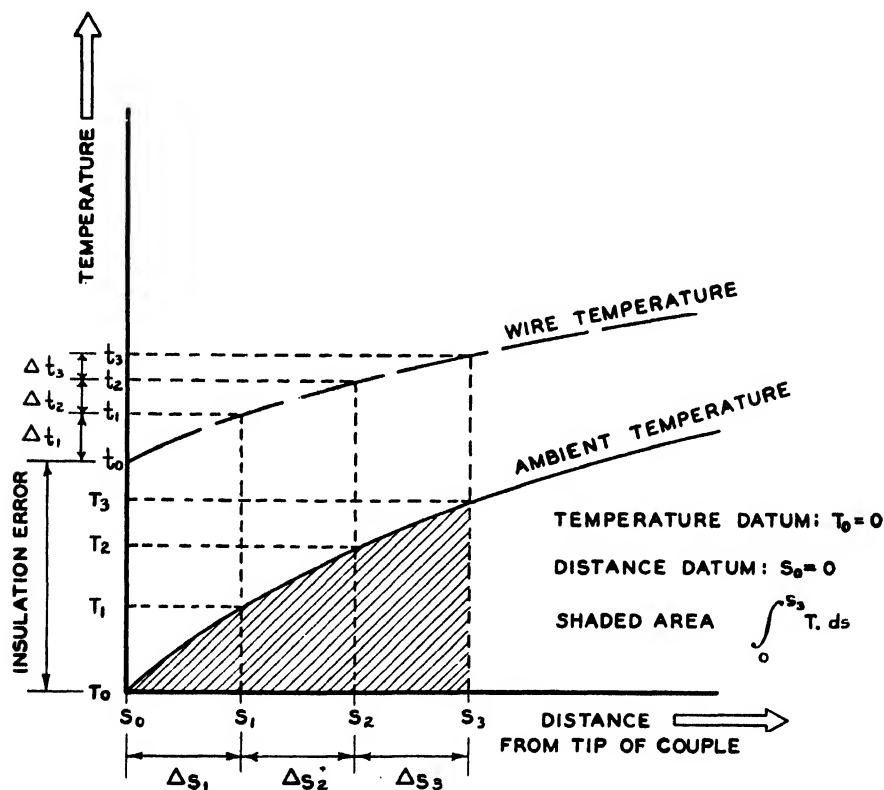


FIG. 6. Sketch illustrating approximate solution of wire temperature equation.

Regrouping, letting $\Delta s_n = \sqrt{2/\phi_n}$ so that the term containing Δt_n disappears, and solving for Δt_{n-1} , we obtain

$$\begin{aligned} \Delta t_{n-1} = \frac{L}{\phi_{n-1} \cdot \Delta s_{n-1} + 2\phi_n \cdot \Delta s_n} \left[\int_0^s \phi \cdot T \cdot ds - \sum_0^{n-2} \phi \cdot \bar{T} \cdot \Delta s \right. \\ \left. - t_{n-2} (\phi_{n-1} \cdot \Delta s_{n-1} + \phi_n \cdot \Delta s_n) - \frac{k t_0}{wK} \right], \end{aligned} \quad (16)$$

in which

$$\Delta s_n = \sqrt{2/\phi_n}. \quad (16a)$$

Equation (16) may be used to calculate Δt for each increment in turn except the first. For example, when $n = 2$, and for a case in which $\phi_1 \cdot \Delta s_1 = \phi_2 \cdot \Delta s_2$, Equation (16) reduces to

$$\Delta t_1 = \frac{0.667}{\phi \cdot \Delta s} \left[\int_0^{s_2} \phi \cdot T \cdot ds - 2\phi \cdot \Delta s \cdot t_0 - k \cdot t_0/w \cdot K \right]. \quad (17)$$

For the first increment, $n = 1$, and Equations (13) and (14) may be combined and reduced to

$$\int_0^{s_1} \phi \cdot T \cdot ds - \phi_1 \cdot \Delta s_1 \cdot t_0 - \frac{k t_0}{wK} = 0, \quad (18)$$

in which

$$\Delta s_1 = \sqrt{2/\phi_1}. \quad (18a)$$

Dividing through by $\phi_1 \cdot \Delta s_1 = \frac{4k \cdot \Delta s_1}{wKD}$, and regrouping

$$t_0 (1 + E) = \frac{1}{\phi_1 \cdot \Delta s_1} \int_0^{s_1} \phi \cdot T \cdot ds \quad (19)$$

where

$$E = \frac{D}{4 \Delta s_1} \text{ is the correction for heat passing through}$$

the end area of the wire,

$$= \sqrt{\frac{Dk}{8wK}}. \quad (20)$$

When $T = F(s)$ may be considered linear over the first increment, Equation (19) reduces to

$$t_0 \approx \frac{1}{2} T_1 / (1 + E). \quad (21)$$

Value of E

Table II lists thermal conductivities of materials commonly used for electrical insulation; the conductivity of copper wire in the same units is about unity. For purposes of illustration, we will assume an average value of $k/K = 5.0 \times 10^{-4}$.

Assuming No. 30 B & S enamelled wire with a diameter of 0.0105 in. outside the insulation and a diameter of 0.0100 in. for the bare wire, the thickness of the insulation may be taken as $w = 0.00025$ in. These values may readily be determined with a traveling microscope in the case of the

TABLE II
THERMAL CONDUCTIVITIES OF INSULATING MATERIALS

10^{-4} cal./ (sec.) (sq. cm.) ($^{\circ}$ C./cm.)

Polyvinyl formal	3.7
Vinyl chloride-acetate	3.9 - 4.0
Rubber	4.3 - 4.5
Gutta percha	4.8
Varnished cloth	5.2
Polyethylene	6.0 - 8.0

Authorities: Miner, "Insulation of Electrical Apparatus," McGraw-Hill, 1941. "Plastics Catalogue," 1946. "Handbook of Physics and Chemistry."

original wire insulation. It is more difficult to estimate the thickness of insulation such as Heresite applied over the tip after soldering the thermocouple.

For such a wire, $E = 0.05$, by Equation (20).

It is evident, therefore, that neglecting the term $(1 + E)$ in Equation (19) or (21) will, in the present example, introduce an error of only 5%, which is so much less than the error that would normally be encountered in estimating k and w for the insulation, that this factor E , to allow for heat entering the wire through its end area, may be neglected. With an equally negligible error the corresponding term $k \cdot t_0/w \cdot K$ may be neglected in the equations where it occurs. It is obvious that there may be cases, particularly with thicker wires, in which E is not negligible, but for simplicity this end effect will be neglected throughout the rest of this paper. Then Equations (1) and (21) reduce to:

$$\text{Insulation error} = t_0 \approx T_1/2. \quad (22)$$

Calculation of Ambient Temperature

The method of calculating the ambient temperature depends, of course, upon the geometry of the thermocouple arrangement employed. Since the case of the chordal hole shown in Fig. 1 is similar to many arrangements commonly used, the ambient temperature curve has been calculated from the tip of the couple to the thermocouple groove. It was assumed that the tip of the couple is 0.500 in. from the surface measured along the axis of the hole, and that the wire is bent down from the axis of the hole at a distance of 0.45 in. from the tip, reaching the bottom of the groove at $s = 0.55$ in. from the tip. The bottom of the groove itself was assumed relatively isothermal over moderate distances, and the flux was taken such as to produce a temperature gradient of 50° F. per inch in the metal wall of the tube.

From the geometry of Fig. 1 it will be obvious that

$$M = \sqrt{N^2 + R^2} - 2N.R. \cos 62^\circ$$

where

$$N = 0.500 - s ;$$

and that

$$T = 50 (0.6112 - M) .$$

The calculated values are shown in Table III and the resulting ambient temperature curve is shown in Fig. 7. This typical ambient temperature curve will be used to illustrate the calculation of wire temperature.

TABLE III
CALCULATION OF AMBIENT TEMPERATURE

Distance from tip s , in.	M , inches	Ambient temperature, T , ° F.
0.00	0.6112	0.00†
0.05	0.5975	0.68
0.10	0.5877	1.18
0.15	0.5820	1.46
0.20	0.5806	1.53
0.25	0.5835	1.38
0.30	0.5906	1.03
0.35	0.6018	0.47
0.40	0.6169	-0.28
0.45	0.6356	-1.22
0.55*	0.5638	2.37

† Temperature datum.

* At bottom of groove, 0.0937 in. deep; $M = 0.6575 - 0.0937$.

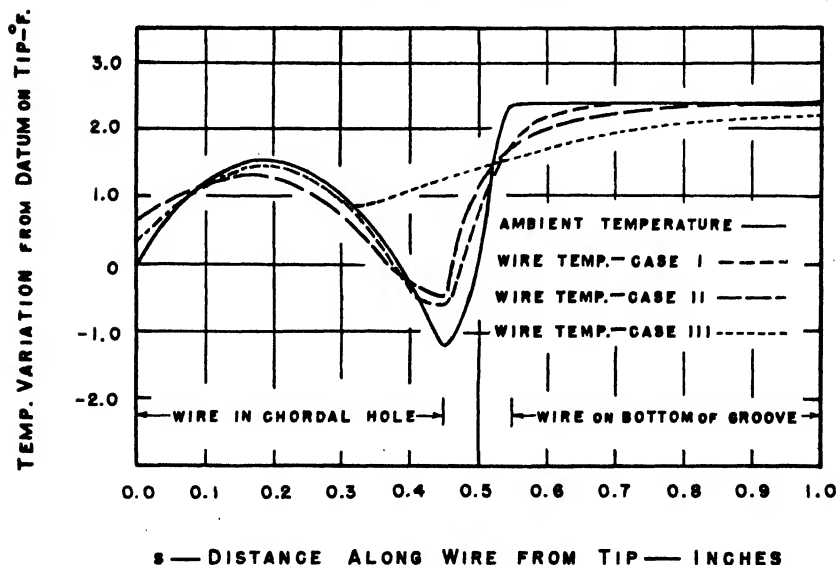


FIG. 7. Typical wire temperature curves.

Calculation of Wire Temperature

In order to give a better understanding of the phenomena involved, the wire temperature has been calculated for three typical cases and the calculations have been carried to several significant figures so that the trends will be clearly shown. The calculation consists of a stepwise solution, one increment at a time, proceeding along the wire from its tip.

Case I

Assume that the insulation throughout the length of the wire is equivalent to the original insulation, 0.00025 in. thick.

Then $\phi = 800 \text{ in.}^{-2}$ by Equation (10a);

$$\Delta s = \sqrt{2/800} = 0.05 \text{ in.}; \text{ and } \phi \cdot \Delta s = 40 \text{ in.}^{-1}$$

The calculations are tabulated in Table IV and the resulting wire temperature curve is plotted in Fig. 7. For the first increment one uses the simplified form of Equation (19), in which end effect is neglected:

$$t_0 = \frac{1}{\phi \cdot \Delta s} \int_0^{s_1} \phi \cdot T \cdot ds \quad (23)$$

And for the second increment one uses the similarly simplified form of Equation (17):

$$\Delta t_1 = \frac{0.667}{\phi \cdot \Delta s} \left[\int_0^{s_2} \phi \cdot T \cdot ds - 2\phi \cdot \Delta s \cdot t_0 \right] \quad (24)$$

For subsequent increments Equation (16), simplified because $\phi \cdot \Delta s$ is constant, is used in the form

$$\Delta t_{n-1} = \frac{0.667}{\phi \cdot \Delta s} \left[\int_0^s \phi \cdot T \cdot ds - \sum_0^{n-2} \phi \cdot \bar{t} \cdot \Delta s - 2\phi \cdot \Delta s \cdot t_{n-2} \right] \quad (25)$$

The first step in the calculation is to fill in the part of the table to the left of the double line, which involves integrating the area under the ambient temperature curve for each increment. In the present work the integration was performed by the primitive but nonetheless satisfactory method of counting squares on the graph paper under the curve in Fig. 7. One then proceeds by working across the table from left to right, completing each line before dropping down to the next. If this systematic procedure is followed, what can be a rather confusing calculation becomes quite straightforward.

As a check on the calculations of Case I, we may apply the criterion provided by Equation (12). The first maximum in the ambient temperature curve occurs at $s = 0.191$ (approx. $n = 4$), and the minimum occurs at $s = 0.450$ ($n = 9$). Applying the criterion, for the first maximum:

$$\int_0^{s_4} \phi \cdot T \cdot ds - \sum_0^4 \phi \cdot \bar{t} \cdot \Delta s = 166.24 - 167.38 = -1.14,$$

and similarly, for the minimum:

$$\int_0^{s_0} \phi \cdot T \cdot ds - \sum_0^0 \phi \cdot \bar{T} \cdot \Delta s = 280.56 - 275.20 = 5.36.$$

TABLE IV
CALCULATION OF WIRE TEMPERATURE CURVE

n	s_n	T_n	$\int_0^s \phi \cdot T \cdot ds$	Δt_{n-1}	t_{n-1}	$\phi \cdot \Delta s \cdot \bar{T}_{n-1}$	$\sum_0^{n-1} \phi \cdot \bar{T} \cdot \Delta s$	$2\phi \cdot \Delta s \cdot t_{n-1}$
<i>Case I</i>								
1	0.05	0.68	14.04	—	0.351	—	—	28.08
2	0.10	1.18	51.88	0.397	0.748	22.00	22.00	59.84
3	0.15	1.46	105.52	0.395	1.143	37.82	59.82	91.44
4	0.20	1.53	166.24	0.250	1.393	50.72	110.54	111.44
5	0.25	1.38	225.32	0.056	1.449	56.84	167.38	115.92
6	0.30	1.03	274.48	-0.147	1.302	55.02	222.40	104.16
7	0.35	0.47	305.40	-0.353	0.949	45.02	267.42	75.92
8	0.40	-0.28	309.92	-0.557	0.392	26.82	294.24	31.36
9	0.45	-1.22	280.56	-0.751	-0.359	0.66	294.90	-28.72
10	0.50	0.10	250.16	-0.267	-0.626	-19.70	275.20	-50.08
11	0.55	2.37	306.04	1.349	0.723	1.94	277.14	57.84
12	0.60	2.37	400.84	1.098	1.821	50.88	328.02	145.68
13	0.65	2.37	495.64	0.366	2.187	80.16	408.18	174.96
14	0.70	2.37	590.44	0.122	2.309	89.92	498.10	184.72
15	0.75	2.37	685.24	0.040	2.349	93.16	591.26	187.92
16	0.80	2.37	780.04	0.014	2.363	94.24	685.50	189.04
17	0.85	2.37	874.84	0.005	2.368	94.62	780.12	189.44
18	0.90	2.37	969.64	0.001	2.369	94.74	874.86	—
<i>Case II</i>								
1	0.10	1.18	12.97	—	0.648	—	—	25.92
2	0.20	1.53	41.56	0.521	1.169	18.17	18.17	46.76
3	0.30	1.03	68.62	0.123	1.292	24.61	42.78	51.68
4	0.40	-0.28	77.48	-0.566	0.726	20.18	62.96	29.04
5	0.50	0.10	62.54	-0.982	-0.256	4.70	67.66	-10.24
6	0.60	2.37	100.21	1.426	1.170	9.14	76.80	46.80
7	0.70	2.37	147.61	0.800	1.970	31.40	108.20	78.80
8	0.80	2.37	195.01	0.267	2.237	42.07	150.27	89.48
9	0.90	2.37	242.41	0.089	2.326	45.63	195.90	93.04
10	1.00	2.37	289.81	0.029	2.355	46.81	242.71	94.20
11	1.10	2.37	337.21	0.010	2.365	47.20	289.91	94.60
12	1.20	2.37	384.61	0.003	2.368	47.33	337.24	—
<i>*Case III</i>								
1	0.05	0.68	14.04	—	0.351	—	—	28.08
2	0.10	1.18	51.88	0.397	0.748	22.00	22.00	59.84
3	0.15	1.46	105.52	0.395	1.143	37.82	59.82	91.44
4	0.20	1.53	166.24	0.250	1.393	50.72	110.54	111.44
5	0.25	1.38	225.32	0.056	1.449	56.84	167.38	115.92
6	0.30	1.03	274.48	-0.147	1.302	55.02	222.40	104.16
7	0.35	0.47	305.40	-0.353	0.949	45.02	267.42	—
8	0.666	2.37	310.92	-0.017	0.932	37.62	305.04	11.78
9	0.982	2.37	325.90	0.958	1.890	8.92	313.96	23.89
10	1.298	2.37	340.88	0.320	2.210	12.96	326.92	27.93
11	1.614	2.37	355.86	0.107	2.317	14.31	341.23	29.28
12	1.930	2.37	370.84	0.035	2.352	14.76	355.99	—

* Case III is identical with Case I down to the heavy line at $s_n = 0.35$, at which point the increase in insulation thickness occurs.

The figure 1.14 is an error of 0.7% at the first maximum, and 5.36 is an error of 2% at the minimum. These errors are primarily due to the assumption on which Equation (14) is based, namely, that the wire temperature curve may be considered linear over the length of each increment. It will be noted that the error introduced by this assumption is not large. An increase in Δs would tend to increase this error, but when an increase in Δs corresponds to an increase in the amount of insulation it tends to make the curve flatter and thereby has a compensating effect.

Case II

Assume that the insulation throughout the length of the wire is 0.001 in. thick. Then $\phi = 200$; $\Delta s = 0.10$; $\phi \cdot \Delta s = 20$.

The calculations here are identical with those for Case I and are as shown in Table IV. The resulting wire temperature curve shown in Fig. 7 indicates the effect of a four-fold increase in insulation thickness as compared with Case I.

It is interesting at this point to compare the values of insulation error obtained by the approximate equation (22) with those obtained by the more accurate form (23). For Case II the approximate equation gives an insulation error $t_0 = 1.18/2 = 0.590^\circ \text{F.}$ compared with the more accurate value of 0.648°F. , an error of 9%. For Case I the corresponding figures are 0.340 and 0.351, an error of 3%. It is obvious, therefore, that the approximate form (Equation 22) may only be used when Δs is relatively short, that is, when the insulation is quite thin.

Case III

Assume the case, illustrated in Fig. 1, in which the insulation thickness is 0.00025 in. from the tip of the wire to the back of the centering bushing—a distance that may be taken as 0.35 in.; and assume that the air or insulation in the drilled hole back of the bushing is equivalent to an insulation thickness of 0.01 in. This case is similar to the installation described in the previous paper (1) and is, therefore, typical of what may be encountered in practice.

The first part of the calculations is identical with that for Case I. For the second section of the wire, $\phi = 20$; $\Delta s = 0.316$; and $\phi \cdot \Delta s = 6.32$. These calculations are also tabulated in Table IV. In the transition from one region to the other, care must be taken to use the correct values of ϕ and of Δs in the equations. Equation (16) must be used for calculating Δt_1 , and $\phi \cdot \Delta s = 40$ must be used in calculating $\phi \cdot \Delta s \cdot t_1$. Otherwise the procedure is identical with that employed for Cases I and II.

Critical Distance

An examination of Fig. 7 shows that the wire temperature approaches the temperature of the thermocouple groove more slowly the thicker the insulation. Similarly, disturbances in the ambient temperature (such as the minimum at $s = 0.45$) have less effect on wire temperature when the insula-

tion is thicker, and the disturbance in wire temperature is then distributed along a greater length of the wire. This indicates qualitatively the fact that the distance along the wire that a disturbance in ambient temperature is transmitted is some function of the thermal resistance of the insulation; it would also be expected to be a function of the conductivity of the wire.

Combining Equations (10a) and (16a) gives just such a relation, namely,

$$\Delta s = \sqrt{\frac{w}{k} \cdot \frac{KD}{2}}, \quad (26)$$

for w/kD is proportional to the thermal resistance of the insulation per unit length of wire, and KD^2 is proportional to the conductivity of the wire per unit of length. We therefore see illustrated what has already been demonstrated by the mathematics of the analysis, namely, that Δs defines the maximum distance that a disturbance at a specific point can be transmitted along the wire. Δs will, therefore, be called the "critical distance."

The significant conclusion is, therefore, reached that the path of the lead wires from the junction need be isothermal only for the critical distance; and if the path is not quite isothermal, then the insulation error is determined by the variation in ambient temperature only over the critical distance.

For Cases I and II above, the critical distances are 0.05 in. and 0.10 in., which are surprisingly short. It is obvious from Equation (26) that the critical distance, and hence the insulation error, is larger, the larger the thermal resistance, w/k , of the insulation. It follows, therefore, that experimenters should strive for a minimum of thermal insulation on the thermocouple wires near the tip without losing the necessary* electrical insulation. Under most circumstances an unusually thick blob of insulation on the tip of a thermocouple could seriously affect the accuracy of the readings. Other factors that will tend to reduce insulation error are small wire diameter and low specific conductivity of wire metal.

Effect of Joining Dissimilar Wires

The discussion thus far has been in terms of a single wire, whereas a thermocouple consists of two dissimilar wires, having different values of K and perhaps of D . Applying Equation (23) will, therefore, give different values, t'_0 and t''_0 , for the two wires. Since the wires are in thermal contact at the tip, their tip temperatures must be identical. In order to establish this equality heat will flow from the wire that is the better conductor into the poorer conductor and the tips will assume a temperature t_0 that is intermediate between t'_0 and t''_0 , the temperature differences being inversely proportional to the conductivities of the wires, thus:

$$\frac{t'_0 - t_0}{t_0 - t''_0} = \frac{K''(D'')^2}{K'(D')^2}.$$

*It is, of course, possible to consider the use of a thermocouple with no insulation at the tip. But insulation simplifies testing; and it is the author's impression that insulated couples are more reliable, although he does not wish to be dogmatic on this point.

Solving this equation gives

$$t_0 = \frac{K'(D')^2 t'_0 + K''(D'')^2 t''_0}{K'(D')^2 + K''(D'')^2} \quad (27)$$

For purposes of illustration constantan may be assumed to have a conductivity one-twentieth that of copper. Consider a copper-constantan thermocouple in which both wires are identical in size and insulation, the values being as in Case I preceding. Then $t'_0 = 0.351^\circ \text{F.}$ for copper (from Table IV), and $K' = 1.00$.

For the constantan wire $\phi = 16,000$; $\Delta s = 0.01118$;

$$\int_0^{s_1} \phi \cdot T \cdot ds = 13.5; t''_0 = 0.075^\circ \text{F.}; \text{ and } K'' = 0.05.$$

$$\text{Then } t_0 = \frac{0.351 + 0.05(0.075)}{1.00 + 0.05} = 0.338^\circ \text{F.}$$

It is evident from the foregoing that, when the thermocouple wires differ greatly in conductivity, the temperature of the junction approaches very closely to that calculated for the better conductor alone. By conductivity is here meant the combined effect of specific conductivity and cross sectional area.

Conclusion

The error in indicated thermocouple temperature due to the presence of the insulation may be eliminated by arranging that the wires follow an isothermal path for a distance from the junction that need not be greater than the critical distance. When the path of the wires is not isothermal the resulting insulation error is determined by the variations in the ambient temperature only over the critical distance from the junction. The magnitude of this critical distance is determined by the relative capacities of the insulation and of the wire metal to conduct heat. The conditions for minimum insulation error are small wire diameter, low specific conductivity of wire metal, thin insulation, and high specific conductivity of the insulation material.

The calculations involved in plotting much of the curve of wire temperature are quite laborious, but are, fortunately, not usually necessary. The calculation of insulation error only is a relatively simple process, the necessary steps being as follows:

- (a) Calculate the critical distance by Equation (26);
- (b) From the geometry of the installation, calculate the ambient temperature T_1 at the critical distance from the junction;
- (c) Calculate insulation error, $t_0 = T_1/2$.

The above procedure assumes that the ambient temperature curve is approximately linear over the critical distance. If greater accuracy is desired the procedure would be:

- (a) Calculate the critical distance by Equation (26);
- (b) From the geometry of the installation, calculate and plot the ambient temperature curve for a little more than the critical distance from the junction;
- (c) With a planimeter or by counting squares, determine the area under the ambient temperature curve for the critical distance from the junction;

- (d) Calculate insulation error, $t_0 = \frac{1}{\Delta s} \int_0^{\Delta s} T. ds.$

The calculated insulation errors in the examples used in this paper have been relatively small since they were based on cases in which insulation thickness and wire diameter were about ideal and since they were for a moderate temperature gradient of 50° F. per inch in the tube wall. Reference to Table I will show that gradients 5 to 10 times as steep may be encountered, giving under the best of conditions insulation errors of the order of a few degrees. Although insulation error is usually not as critical as the geometric errors described in the previous paper (1), it can be excessive if adequate precautions are not taken.

It is hoped that, in the future, authors reporting the results of heat transfer film coefficient measurements will calculate and report the values of geometric and insulation errors so that the accuracy of their data will be established.

Table of Nomenclature

- D = diameter of thermocouple lead wire.
- E = term to correct for heat entering end area of wire.
- k = specific conductivity of wire insulation.
- K = specific conductivity of wire metal.
- M = distance from center of tube to any given point in the wire.
- N = distance from surface of tube to same point in the wire as defines M , see Fig. 1.
- Q = quantity of heat flowing across any given cross section of the wire.
- Q' = quantity of heat flowing into wire through its end area.
- R = radius of the tube.
- s = distance measured along the thermocouple wire.

- Δs = length of increment of wire; more specifically, Δs is "critical distance" = $\sqrt{2/\phi}$.
- t = temperature at any given point in the thermocouple wire, i.e. "wire temperature."
- \bar{t} = average value of t for any given increment of the wire.
- t_0 = wire temperature at the tip or junction; by choice of temperature datum t_0 is also equal to the insulation error.
- T = average temperature of the surrounding tube metal to which any given cross section of the wire is subjected, i.e., "ambient temperature."
- T_0 = ambient temperature at the tip or junction; $T_0 = 0$ by choice of datum temperature.
- T_1 = ambient temperature at a distance $\Delta s_1 = \sqrt{2/\phi}$ from the tip or junction.
- T_θ = temperature at any point on the periphery of the wire.
- ΔT_i = temperature difference across the insulation of the wire at any point on its periphery; $\overline{\Delta T_i}$ is average of values around the periphery at any given cross section.
- x = distance measured across the diameter of the wire from the hotter side.
- w = thickness of wire insulation.
- α = temperature gradient in the tube wall.
- ϕ = a coefficient defined by Equation (10a)
- θ = angle defining position of a point on periphery of wire, see Fig. 3
- Primes: ' and '' indicate different values for two dissimilar metals forming a thermocouple, e.g., for copper and for constantan.

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